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VOL. XXXV] *SECTION A* [No. 1

JANUARY 1952

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PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, BANGALORE.

# TAMARIND SEED JELLOSE[1] : FERMENTATIVE DEGRADATION

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Received September 14, 1951

It has already been reported by Rao, Ghose and Krishna[2] that tamarind seed jellose undergoes complete hydrolysis when boiled with 5 per cent. sulphuric acid for 4 hours, yielding xylose, glucose and galactose. Experiments on the fermentative degradation of the jellose under the influence of fungus have now been carried out, with a view to obtaining the probable structural unit of which the jellose molecule is built.

The fungus is initiated by exposing a solution of the jellose to air for a few moments. After incubation it develops on the surface of the solution into a greenish-grey velvety mat consisting mostly of *Cladosporium herbarum* (Pers.) Link. The colony, after establishment in malt agar, is used as inoculum for subsequent experiments.

Under the action of this culture, an aqueous solution of tamarind seed jellose undergoes fermentative degradation. Amongst the degradation products is found a hexasaccharide. This carbohydrate, which may be called *Tamarindose*, differs in its properties from the original jellose as shown below:—

| | The original jellose | The degradation product |
|---|---|---|
| Appearance .. | Amorphous | Microcrystalline |
| Solubility : | | |
| (*a*) Water .. | Colloidal solution | Clear solution |
| (*b*) 70% alcohol .. | Insoluble | Soluble |
| Specific rotation .. | +71·4° | +73·8° |
| Fehling's solution .. | Blue gelatinous precipitate | Reduced to cuprous oxide |
| Iodine .. | Blue gel in strong solutions ; pale yellow on dilution | No apparent action |
| Borax .. | A thick jelly | No action |
| Sugar .. | A firm jelly | No action |
| Sugar and citric acid .. | A firm jelly | No action |
| Molecular weight .. | Very high | About 975 |

The carbohydrate nature of the compound is indicated by its response to the characteristic Dreywood reaction by developing a green colour on treatment with anthrone and sulphuric acid.[3] It is a reducing carbohydrate

and its reducing power of the Fehling's solution corresponds to that of a hexasaccharide. It undergoes complete hydrolysis when boiled with 4 per cent. sulphuric acid for 3 hours and yields 107·2 per cent. of reducing sugars expressed as glucose. The hydrolysate contains only xylose, galactose and glucose, and quantitative estimations show that the first two sugars are 30·0 and 16·7 per cent. respectively, so that glucose comes to 53·3 per cent. by difference. These percentages approximately correspond to the molecular proportion of 2 of xylose, 1 of galactose and 3 of glucose. The molecular weight is determined by employing Kiliani reaction, modifying slightly the procedure recommended by Militzer for quantitative estimation of sugars,[4] and, though slightly higher, it seems to offer support to the hexasaccharide formula. It appears, therefore, that tamarindose is a hexasaccharide composed of xylose, galactose and glucose in the molecular proportion of 2 : 1 : 3.

The hexasaccharide undergoes acetylation easily when boiled with acetic anhydride and anhydrous sodium acetate, and the product which is freely soluble in acetone, alcohol, chloroform, acetic acid, etc., has a specific rotation of 43·6° in methyl alcoholic solution at 30° C.

The question of the relative proportion of the constituting sugars in the original jellose has also been reexamined now. From the specific rotation of the hydrolysate it was originally suggested by Rao, *et. al.*[2] that the sugars might be present in equimolecular proportion, while Savur and Sreenivasan[5] concluded from quantitative estimations that xylose, galactose and glucose corresponded approximately to the molecular proportion of 2 : 1 : 3. The percentage of xylosan had already been reported to be 30·5 from these laboratories.[2] Galactan has now been estimated and is found to be 17·2 per cent. Making calculations on the basis of pure anhydrous jellose, the glucosan in it comes by difference to be 52·3 per cent. These results are in agreement with those reported by Savur and Sreenivasan.[5]

## EXPERIMENTAL

*Preparation of tamarindose.*—A 2 per cent. solution of tamarind seed jellose was sterilised for 15 minutes at 15 lbs. pressure, and when cooled the sterile solution was exposed to air for a few moments during the month of June, when the local maximum and minimum temperatures were respectively 100° F. and 75° F. and the relative humidity was 50 per cent. After incubation for about a week at 30° C., a greenish-grey velvety mat appeared on the surface of the solution. The colony which was found to consist mostly of the hyphæ and spores of *Cladosporium herbarum* was established in a culture medium consisting of 2·5 g. of malt and 2·0 g. of agar in 100 c.c.

of distilled water. This culture was used as inoculum for subsequent experiments.

For the isolation of tamarindose, a litre of a 2 per cent. solution of crude tamarind seed jellose was sterilised as before, and was inoculated with the fungus colony. It was kept in an incubator at 30° C. During the first 2 or 3 days, a sediment settled down at the bottom of the flask and the fungus which grew very rapidly spread itself into a mat on the surface of the solution. The latter became thinner and thinner as the fermentation progressed and there was also a fall in the pH at the rate of 0·1 per day. When the pH value fell to 4·9, which happened in about 2 weeks, the solution became quite watery and transparent. It was then filtered through fluted filters and concentrated on a water-bath to about 200 c.c. It was then boiled with a little animal charcoal in order to remove the colloidal impurities still present and also the small amount of colour that developed during concentration. The clear solution was then treated with 3 times its volume of 95 per cent. alcohol, filtered, and distilled under vacuum. When the solution assumed a syrupy consistency, it was transferred into a porcelain basin and the evaporation continued in a vacuum desiccator. For purification, a concentrated aqueous solution of the solid was treated with twice its volume of absolute alcohol, filtered, and concentrated as before in vacuum. For crystallization a concentrated aqueous solution of the compound was treated with absolute alcohol till opalescence appeared, filtered and then kept in a stoppered flask, when solid separated out gradually as microcrystalline rectangular plates. From 20 g. of the crude jellose, 8 g. of tamarindose were obtained.

The carbohydrate was freely soluble in water and 70 per cent. alcohol, moderately soluble in glacial acetic acid and insoluble in absolute alcohol. On heating it shrank and sintered at 100–10° C. (dehydration) and the anhydrous material decomposed at 228–30° C. It was more insipid than sweet in taste. (Found in the sample dried at 105° C. under vacuum: C, 43·90; H, 6·80; $C_{34}H_{58}O_{29}$ requires C, 43·87; H, 6·24 per cent.) The crystals seemed to possess 6 molecules of water of crystallization. (Loss on heating at 105° under vacuum: 10·8; $C_{34}H_{58}O_{29}$, 6 $H_2O$ requires a loss of 10·4 per cent. on dehydration.) Its aqueous solution was dextrorotatory, the specific rotation, $[\alpha]_D^{30°}$, being 73·8°. It reduced Fehling's solution, 100 mg. liberating 38 to 40 mg. of cuprous oxide.

*Hydrolysis.*—1 g. of a purified sample of tamarindose was heated for 3 hours with 50 c.c. of 4 per cent. sulphuric acid at the temperature of boiling water bath. After cooling the clear solution was neutralized with sodium

carbonate, the volume made upto 100 c.c. and the reducing sugars were estimated. Calculated as glucose, the sugars totalled 107·2 per cent. on the basis of anhydrous material.

The only sugars that could be identified in the hydrolysate were xylose, galactose and glucose. When a neutral solution was treated with phenyl hydrazine in the usual way, a mixture of the osazones separated out, the first fraction being xylosazone and the last fraction galactosazone. The presence of xylose was confirmed by the preparation of the characteristic dibenzylidene dimethyl acetal derivative according to the method of Breddy and Jones.[6] A small quantity (0·5 g.) of the perfectly dry product of hydrolysis was treated in a dry flask with 10 c.c. of a reagent prepared by dissolving benzaldehyde (40 c.c.) in a mixture of 2·6 N methanolic hydrogen chloride (20 c.c.) and anhydrous methanol (120 c.c.). The mixture was left at the laboratory temperature with frequent shaking. The substance went into solution during the course of 2 days and then the derivative began to separate out gradually. The deposition was complete after the 7th day. It was filtered, washed successively with water (200 c.c.) and methanol (40 c.c.). It was obtained as narrow rectangular plates, some of them tapering at the ends, and melted at 210–11° C. Mixed melting point with an authentic sample prepared from pure xylose was undepressed.

*Xylose content.*—The xylose content was estimated according to the method of Krober as modified by Angell, Norris and Resch[7]. 0·5 g. of tamarindose was taken and distilled with 100 c.c. of 12 per cent. hydrochloric acid over a glycerol bath at 175–80° C. More of 12 per cent. hydrochloric acid was added gradually so that the original volume was maintained as the distillation continued. 360 c.c. of the distillate were collected in about 2 hours, filtered and then treated with 0·5 g. of phloroglucinol dissolved in hydrochloric acid. The precipitate was allowed to stand overnight, filtered in a glass-sintered crucible and weighed after drying. From the amount of the phloroglucide obtained, the xylose content was calculated and found to be 30·0 per cent.

*Galactose content.*—The galactose content was estimated according to the method of Tollens.[8] 5 g. of tamarindose were treated with 50 c.c. of nitric acid of sp. gr. 1·15 in a beaker, 6 cm. in diameter, and the solution was concentrated to one-third of its volume on a water bath. After cooling, the solution was diluted with 100 c.c. of water and then seeded with 0·5 g. of pure mucic acid to facilitate the crystallization of the mucic acid formed during the oxidation. After 2 days' standing with occasional stirring the solid that separated out was collected on a weighed filter, washed twice

with 5 c.c. of cold water, dried at 100°C. and weighed. 0·57 g. of mucic acid was obtained which was equivalent to 0·74 g. of galactose. Hence the galactose present in tamarindose on the basis of anhydrous material was 16·7 per cent.

*Molecular weight estimation.*—The carbohydrate (2 g.) was dissolved in 18 c.c. of 0·1 N acetic acid in a glass-stoppered 250 c.c. Erlenmeyer flask and treated with 20 c.c. of 0·2 N potassium cyanide solution. The reaction flask was immediately stoppered, sealed with glycerol and kept in a cool place for 24 hours. After this period the stopper was carefully removed, and about 20 c.c. of 6 N ammonium hydroxide were added. The stopper was replaced for a few minutes and the flask shaken well for a good mixing. After adding 0·2 g. of potassium iodide the solution was titrated to the first perceptible turbidity with 0·1 N silver nitrate. A blank was also run simultaneously. The difference in the titre values between the blank and the sample experiment multiplied by 13 represented the number of milligrams of potassium cyanide consumed by the carbohydrate, and it came to be 118·4 milligrams. Hence the molecular weight of the carbohydrate would be 975 nearly. A hexasaccharide composed of two molecules of xylose, one of galactose and three of glucose, ($C_{34}H_{58}O_{29}$), requires 930 for its molecular weight.

*Acetyl tamarindose.*—Tamarindose underwent easy acetylation when treated with acetic anhydride and anhydrous sodium acetate for 4 hours at the temperature of water-bath. The acetyl derivative was soluble in methyl and ethyl alcohols, acetic acid, acetone, etc., but heating with hydroxy solvents like alcohol and acetic acid brought about its decomposition. For purification the substance was dissolved in chloroform and the solution was treated with petroleum ether in drops. All the impurities separated out first as a brownish oily liquid. After the removal of the oily liquid, the chloroform solution was further diluted with petroleum ether, when acetyl tamarindose separated as a colourless fluffy precipitate. For crystallization the dry acetate was dissolved in hot acetic anhydride and the solution treated in the cold with an equal amount of absolute alcohol. After two days the acetate separated as a microcrystalline powder. On heating it sintered at 154° C., became glassy as the temperature was raised and decomposed at 172–74° C. In methyl alcoholic solution its specific rotation was 43·6° at 30° C. (Found: C, 50·37; H, 5·98; $C_{34}H_{40}O_{11}$ $(OCOCH_3)_{18}$ requires C, 49·82; H, 5·58 per cent.) The acetyl group was estimated according to the method of Eberstadt.[9] (Found: $-COCH_3$, 46·45; $C_{34}H_{40}O_{11}$ $(OCOCH_3)_{18}$ requires $-COCH_3$, 45·91 per cent.)

*Galactan content of the jellose.*—The estimation was carried out according to the method of Tollens as described under tamarindose. The weight of mucic acid formed multiplied by 1·197 gave the amount of galactan. From 5 g. of the pure dry material 0·72 g. of mucic acid was obtained so that the jellose contained 17·2 per cent. of galactan.

## SUMMARY

Tamarind seed jellose undergoes fermentative degradation in aqueous solution yielding a hexasaccharide which is composed of xylose, galactose and glucose in the molecular proportion of 2:1:3. The carbohydrate, which may be named Tamarindose, decomposes at 228–30° C. and has a specific rotation of + 73·8° at 30°. Its acetate melts with decomposition at 172–74° and has a specific rotation of + 43·6° in methyl alcoholic solution at 30°.

## ACKNOWLEDGMENT

Our thanks are due to Dr. K. Bagchee and Dr. B. K. Bakshi of the Mycology Branch of this Institute for their kind help in the conduct of the biological aspects of the investigation. They are also due to Dr. S. Krishna, the late Vice-President of this Institute, for his interest in this work.

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# OXIDATION BY CHLORAMINE-T

## Part I. Reaction between Hydrogen Sulphide and Chloramine-T

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Received February 12, 1951

### Introduction

As early as 1905 Chattaway[1] observed that sulphonchloro amides take part in certain characteristic reactions, which show the presence of nitrogen-halogen linkages in their molecule. In such reactions, the halogen is replaced by hydrogen, and sulphonamide is regenerated. Chattaway also showed that sulphur was set free when hydrogen sulphide was treated with chloramine-T.

Coull, Hope and Gouguell[2] investigated the kinetics of the reaction between hydrogen peroxide and chloramine-T, in presence of hydrochloric acid. They suggested the existence of opposing reactions and developed a differential equation expressing the over-all rate of reaction between chloramine-T and hydrogen peroxide.

Afans'ev[3] studied the mechanism of the oxidation of chloramine-T and concluded that in neutral solutions, the oxidising action was due to the hypochlorite ion while in acid solutions, free hypochlorous acid itself, functioned as the oxidant.

Bendall, Mann and Purdie[4] found that, when an excess of hydrogen sulphide was passed into an aqueous solution of chloramine-T, sulphuric acid (with a trace of sulphur) was formed. They also observed that sulphuric acid was the main product, when a dilute solution of chloramine-T was titrated with aqueous hydrogen sulphide. On the other hand, when the titration was carried out with sodium sulphide, the principal product of oxidation was sulphur and the solution was markedly alkaline. Even when an excess of chloramine-T was used in the latter reaction, sulphur continued to be the main product, indicating thereby, that the freshly deposited sulphur was not oxidised by the reagent. From these results, they came to the conclusion that the oxidation of hydrogen sulphide was distinct from that of the sulphide ion and that elemental sulphur could not be an intermediate stage in the oxidation of hydrogen sulphide to sulphuric acid.

* This paper is a revised form of a part of the thesis of A. R. V. Murthy, accepted for the M.Sc. degree of the Mysore University. The investigation was conducted at the Central College, Bangalore.

Choppin and Faulkenberry[5] carried out a systematic investigation of the oxidation of aqueous sulphide solutions by hypochlorites and found that the pH of the system affected the nature of the product of oxidation.

In the present study, it was observed that the nature of the products of the reaction between hydrogen sulphide and chloramine-T largely depended on the pH of the solution and that only sulphur and sulphuric acid were produced. Investigations were conducted to elucidate the nature of the phenomenon.

## EXPERIMENTAL

*Hydrogen sulphide.*—Hydrogen sulphide was prepared by the action of water on aluminium sulphide. The gas was frozen by liquid air, the impurities pumped off, and the solid allowed to evaporate. The gas was collected and stored in glass globes.

*Chloramine-T.*—Chloramine-T was recrystallised from hot water. The crystals, on analysis, were found to be pure trihydrate. The aqueous solution of chloramine-T was standardised iodometrically before use.

*Buffers.*—For the lower pH values, hydrochloric acid—sodium acetate buffers were used while for higher pH values, phosphate-borax and borax-alkali buffers were employed.[6]

A solution of chloramine-T was quite clear in alkaline buffers but was turbid at pH 5·8. On further lowering of pH, the turbidity increased.

The apparatus shown in Fig. 1 was employed.

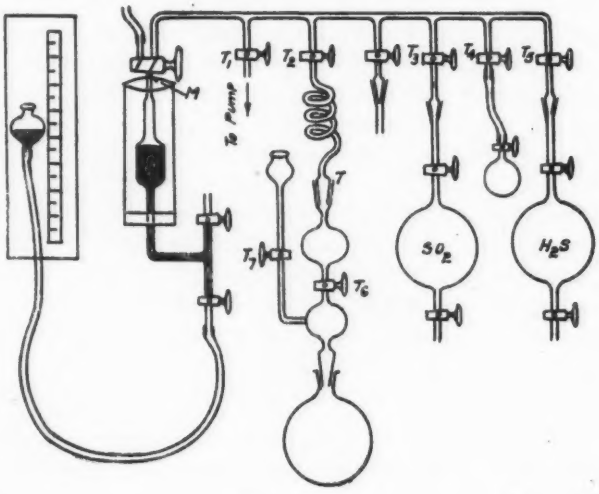


FIG. 1

The reaction vessel, along with the gas burette, was evacuated ($T_1$, $T_2$ and $T_6$ being open and the rest of the stop cocks closed) and was tested for leakage. $T_1$ and $T_2$ were then closed and an appropriate volume of hydrogen sulphide from the globe was let into the graduated tube through the tap $T_5$. The mercury level was adjusted to the mark and the reading on the graduated scale noted down. Then, tap $T_2$ was opened and the mercury level gradually raised, driving the gas slowly into the reaction vessel. When the mercury level came to the mark M, the tap $T_2$ was closed. The mercury level was once again brought to the original mark, and the reading noted, the difference between the two readings being the pressure of the gas employed for the reaction with chloramine-T.

Twenty ml. of 0·2 N chloramine-T was mixed with an equal volume of the selected buffer. The reagent was introduced into the flask through the tap $T_7$. An appropriate correction was applied for the very small amount of hydrogen sulphide left over in the gas burette.

After about half an hour, taps $T_2$ and $T_6$ were closed, and the reaction vessel was taken out, and shaken well. A known volume of standard sodium arsenite solution was added and the arsenite left over after reaction with the residual chloramine-T was determined iodometrically in presence of sodium bicarbonate. It has already been stated that sulphur and sulphuric acid are the only products of oxidation of hydrogen sulphide by chloramine-T. On this basis, the extent of each of the two types of oxidation can be calculated from the volume of hydrogen sulphide employed, and the chloramine-T consumed, the equations being:—

$$a + b = y$$

$$a + 4b = 1{\cdot}12\,x$$

where

$y$ = ml. of $H_2S$ (at N.T.P.) oxidised,

$a$ = ml. of $H_2S$ oxidised to sulphur,

$b$ = ml. of. $H_2S$ oxidised to sulphuric acid,

$x$ = ml. of 0·1 N chloramine-T consumed by the hydrogen sulphide

The following table gives the extent of each of the two reactions, at various pH values,

*Reaction between Hydrogen Sulphide and Chloramine-T*

| Sl. No. | pH of solution | Buffer used | Value of '*a*' | Value of '*b*' | Ratio of *b* to *a* | Remarks |
|---|---|---|---|---|---|---|
| 1 | Soln. highly acid (2 N $H_2SO_4$) | | 0·08 | 7·48 | Complete oxidation to sulphuric acid | |
| 2 | 0·65 | Acetate | 0·46 | 7·65 | 16·6 | |
| 3 | ,, | ,, | 0·8 | 6·4 | 8·0 | Reaction in presence of platinised asbestos |
| 4 | 2·64 | ,, | 0·67 | 7·28 | 10·9 | |
| 5 | 4·76 | ,, | 0·81 | 6·95 | 8·6 | |
| 6 | 4·76 | ,, +2 ml. of sodium molybdate | 0·54 | 6·74 | 12·5 | |
| 7 | 4·76 | ,, +10 ml. of sodium molybdate | 0·61 | 7·06 | 11·6 | |
| 8 | 4·76 | ,, +0·5 ml. of sodium molybdare | 0·55 | 6·6 | 12·0 | |
| 9 | 7·0 | Phosphate | 2·8 | 4·53 | 1·6 | |
| 10 | 7·0 | ,, +brucine | 3·66 | 3·69 | 1·0 | |
| 11 | 7·0 | ,, +osmic acid | 3·52 | 3·56 | 1·0 | |
| 12 | 7·0 | ,, +2 ml. of sodium molybdate | 1·9 | 5·37 | 2·8 | |
| 13 | 7·0 | ,, +2 ml. of sodium molybdate | 2·04 | 4·98 | 2·4 | |
| 14 | 7·0 | ,, +10 ml. of sodium molybdate | 2·07 | 4·98 | 2·4 | |
| 15 | 7·0 | ,, +0·5 ml of sodium molybdate | 2·11 | 2·99 | 2·4 | |
| 16 | 7·0 | ,, +5 g. of sodium chloride | 2·69 | 4·59 | 1·7 | |
| 17 | 7·0 | ,, +5 g. of sodium chloride + 2 ml. of sodium molybdate | 1·97 | 5·41 | 2·9 | |
| 18 | 7·0 | Borate | 2·38 | 4·79 | 2·0 | |
| 19 | 7·0 | ,, +2 ml. of sodium molybdate | 1·69 | 5·66 | 3·4 | |
| 20 | 7·0 | ,, +10 ml. of sodium molybdate | 1·69 | 5·6 | 3·3 | |
| 21 | 7·0 | Phosphate + 2 ml. of sodium tungstate* | 4·59 | 2·55 | 0·55 | |
| 22 | 9·2 | Borax | 4·36 | 3·63 | 0·83 | |
| 23 | 9·2 | ,, | 4·30 | 3·6 | 0·85 | |
| 24 | 9·2 | ,, +10 ml. of sodium molybdate | 4·31 | 3·62 | 0·66 | |
| 25 | 12 | Borate | 8·36 | 0·16 | 0·02 | |

* The sodium molybdate and the soduim tungstate solutions had 5% (by wt.) of the dihydrate of the salt.

## DISCUSSION

The experimental results recorded in this paper can be explained on the basis of the formation of dihydrogen sulphoxide ($H_2SO$) as the primary product of oxidation of hydrogen sulphide. Bendall and coworkers[4] also considered the sulphoxide to be a possible intermediate product in the oxidation of hydrogen sulphide by chloramine-T. They attempted to isolate

the sulphoxide but were unsuccessful. They attributed their failure, to further oxidation of the intermediate product, at a very rapid rate.

Dihydrogen sulphoxide, it may be pointed out, would resemble hydrogen peroxide and hydrogen persulphide in its properties and would therefore be highly unstable. The inability of Bendall *et al.* to isolate the sulphoxide is, in our opinion, due to the high instability of the sulphoxide, rather than to its rapid oxidation to sulphate.

It is well known that the peroxide and the persulphide of hydrogen are catalytically decomposed by a variety of substances. Hydrogen ion has a stabilising influence on the two compounds while hydroxyl ion brings about their rapid decomposition. The sulphoxide would presumably behave in a similar way towards catalysts.

Dihydrogen sulphoxide can undergo two simultaneous reactions—a decomposition (Reaction A) and an oxidation (Reaction B):—

$$H_2SO \longrightarrow H_2O + S \quad \text{(Reaction A)}$$

$$H_2SO \xrightarrow{O} H_2SO_4 \quad \text{(Reaction B)}$$

At low pH, owing to the greater stability of the sulphoxide, Reaction A would take place to a much smaller extent than Reaction B. As the pH increases however, the stability of the sulphoxide decreases and at high pH values, it decomposes so readily as not to admit of any appreciable oxidation. Therefore, as the pH increases, there is a progressive increase in the value of "a" and a corresponding decrease in the value of "b".

It has to be pointed out, that only the unionised hydrogen sulphide is likely to form the sulphoxide on oxidation. In the case of sulphide ions, the oxidation would consist of loss of electrons by the ions to give rise to elemental sulphur. In solutions in which the hydrogen sulphide was partly ionised, sulphur liberation would be due to two causes:—(i) oxidation of sulphide ion and (ii) decomposition of dihydrogen sulphoxide.

The liberated sulphur is not appreciably oxidised by chloramine-T even when the oxidant is in large excess, as noticed by Bendall *et al.*[4] Oxidation of elemental sulphur would however, take place in highly alkaline solutions of hypochlorite. The sulphur would first react with the alkali to form sulphide and thiosulphate, and these products would then be oxidised by the hypochlorite, as pointed out by Choppin and Faulkenberry.[5] Willard and Cake[7] noticed that for the quantitative oxidation of sulphide to sulphate the hypochlorite was to be in large excess and that the solution should be about 4 N in regard to the alkali.

From the experimental data obtained by Choppin and Faulkenberry[5] it is clear that the oxidation of sulphur to sulphate by the hypochlorite, is noticeable only at a pH higher than 10. As has been pointed out earlier in the paper, the active principle of chloramine-T as an oxidant, is probably hypochlorous acid or its anion (Afans'ev[3]). A close agreement between the results of the present investigation (wherein chloramine-T has been used) and those obtained by Choppin and Faulkenberry with hypochlorite is therefore to be expected. Such agreement is indeed quite noticeable. With the exception of borate buffer of pH 12, the solutions employed by us were all of a pH lower than 10 and the chances of oxidation of primarily formed sulphur to sulphate could therefore be ruled out.

It has already been indicated that catalysts would influence the stability of dihydrogen sulphoxide. Such catalysts would consequently affect the relative magnitude of the two reactions A and B. This is clearly noticeable in the case of solutions of pH 7·0. The sulphate and sulphur produced in these experiments, varied with the composition of the solution. The presence of molybdate considerably raised sulphate formation, while sodium tungstate markedly reduced the oxidation of sulphate or possibly hastened the decomposition of hydrogen sulphoxide. Brucine and osmic acid seemed to have the same effect as the tungstate, though to a smaller extent. It is significant that in presence of platinised asbestos, relatively more sulphur is produced. Finely divided platinum is known to decompose hydrogen peroxide and can be expected to have a similar effect on dihydrogen sulphoxide.

## SUMMARY

When hydrogen sulphide is oxidised by chloramine-T, the sulphide may yield sulphur, or sulphate, or both the products. The relative proportion of the two products of oxidation depends on the pH, of the solution and on the presence of certain catalysts. At low pH, sulphate is produced in relatively high amounts, while at higher pH values, sulphur formation is greater. Presence of molybdate increases sulphate yield, while tungstate on the other hand, diminishes it. It is suggested that the primary product of oxidation of hydrogen sulphide is dihydrogen sulphoxide ($H_2SO$) which, being analogous to hydrogen peroxide and hydrogen persulphide, is likely to be more stable at low pH values. The sulphoxide undergoes two simultaneous reactions, (*a*) decomposition into water and sulphur and (*b*) oxidation to sulphate. This accounts for the greater production of sulphate at low pH values, and of elemental sulphur in alkaline solutions.

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# NOTE ON THE PERTURBATION CALCULATION OF PHASE SHIFTS FOR CENTRAL AND NON-CENTRAL INTERACTIONS*

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Received October 31, 1951

(Communicated by Dr. K. R. Ramanathan, F.A.SC.)

## Introduction

It is well known that the mutual scattering of two particles is completely determined by the asymptotic phase shifts in the appropriate wave function. The purpose of this note is to point out that the calculation of the phase shifts can be reduced to an ordinary eigenvalue problem (for a closed state). By applying the usual perturbation theory to the latter, one obtains readily the phase shifts as series in powers of the interaction potential;† the first order term is, as is to be expected, identical with Born's approximation. The procedure, it will be shown, is applicable to non-central as well as centrally symmetric interactions.

## 2. Centrally Symmetric Interactions

Consider first scatterings due to centrally symmetric interactions. For discussing the motion in the centre of gravity system, one can regard one of the scattering partners as a fixed scattering centre and the other as the scattered particle having the reduced mass $\mu$ of the system. Let us imagine the latter particle enclosed in a large empty sphere (radius R) and work out the shifts of its energy levels when the scattering centre is introduced at the centre of the sphere. For a state with the orbital quantum number $l$, the asymptotic radial wave functions with and without the scattering centre are respectively:

$$\sim \frac{1}{r} \sin (kr - l\pi/2 + \eta_l), \qquad (a)$$

$$\sim \frac{1}{r} \sin (kr - l\pi/2) \qquad (b) \qquad (1)$$

* This work was completed while the authors were at the Department of Theoretical Physics, University of Liverpool.

† For an elegant discussion on the convergence of Born's expansion see Jost & Pais (1951).

where $\eta_l$ is the phase shift required for the scattering problem and $k$ is the wave number of the particle in the centre of mass system. Clearly the wave number $k$ must in either case be such that the wave function has a node at $r = R$ (the corresponding eigenvalue $= \hbar^2 k^2/2\mu$). Consequently the difference of $k$ in the two cases must be exactly so as to compensate for the appearance of the phase shift in (*a*), thus,

$$R\,\Delta k = -\eta_l \tag{2}$$

As $R \to \infty$, $\Delta k$ is infinitesimal, hence the shift in the eigenvalue is given by

$$\Delta E = \Delta\left(\frac{\hbar^2 k^2}{2\mu}\right) = \frac{\hbar^2 k}{\mu}\,\Delta k = -\frac{\hbar^2 k \eta_l}{R\mu}. \tag{3}$$

The phase shifts have thus been expressed in terms of eigenvalues of certain closed states.

The series expansion for $\eta_l$ follows directly, when one considers the interaction potential as a perturbation and applies the usual perturbation theory to determine the energy shift $\Delta E$. When properly normalized for sufficiently larger $R$, the unperturbed radial wave functions are given by

$$R_{kl}^{0}(r) = \left(\frac{\pi k}{Rr}\right)^{\frac{1}{2}} J_{(l+\frac{1}{2})}(kr), \tag{4}$$

where $J_{(l+\frac{1}{2})}(kr)$ are the half integral Bessel functions. Making use of (4) one obtains, for instance, the first and second order terms of $\eta_l$ explicitly as

$$\eta_{kl}^{(1)} = -(\mu\pi/\hbar^2) \int_0^\infty J^2_{(l+\frac{1}{2})}(kr)\, V(r)\, r\,dr \tag{5}$$

$$\eta_{kl}^{(2)} = -\left(\frac{2\pi^2\mu^2}{\hbar^4 R}\right) \sum_{k' \neq k} \frac{k'}{k^2 - k'^2} \left\{ \int_0^\infty J_{(l+\frac{1}{2})}(kr)\,(r)\, J_{(l+\frac{1}{2})}(k'r)\, r\,dr \right\}^2$$

$$= -\frac{2\pi\mu^2}{\hbar^4} \int_0^\infty \left[ \frac{k'\,dk'}{k'^2 - k^2} \left\{ \int_0^\infty J_{(l+\frac{1}{2})}(kr)\, V(r)\, J_{(l+\frac{1}{2})}(k'r)\, r\,dr \right\} \times \right.$$

$$\left. \times \left\{ \int_0^\infty J_{-(l+\frac{1}{2})}(kr')\, V(r')\, J_{(l+\frac{1}{2})}(k'r')\, r'\,dr' \right\} \right]$$

$$= (-1)^l \left(\frac{2\pi^2\mu^2}{\hbar^4}\right) \int_0^\infty J_{(l+\frac{1}{2})}(kr)\, V(r)\, J_{-(l+\frac{1}{2})}(kr)\, r\,dr \times$$

$$\times \int_0^r J^2_{(l+\frac{1}{2})}(kr')\, V(r')\, r'\,dr', \tag{6}$$

where, for the large $R$ assumed, the summation over $k'$ has become an integral; for the latter, it is clear from the way it has been derived that Cauchy's principal value should be taken. The result of the corresponding integration, namely,

$$\int_0^\infty \frac{J_{(l+\frac{1}{2})}(k'r)\, J_{(l+\frac{1}{2})}(k'r')\, k'dk'}{k'^2 - k^2} = (-1)^l \left(\frac{\pi}{2}\right) J_{(l+\frac{1}{2})}(kr)\, J_{(l+\frac{1}{2})}(kr') \quad (7)$$

for $r' > r$, is obtained with the help of a contour integral which is an easy modification of an example given in Watson's book (1944) on Bessel functions.

The first order expression, we observe, is identical with Born's approximation. Using relatively involved methods, similar expansions for the phase shifts have been obtained by Hellund (1941) for central interactions. His second order expression (28) after correcting a slight misprint, in that the last Bessel function occurring in (28) should read $J_{(l+\frac{1}{2})}(kr)$ instead of $J_{-(l+\frac{1}{2})}(kr)$ can be easily seen to be identical with our expression (6).

## 3. NON-CENTRAL INTERACTIONS

For non-central forces, we shall consider as an example the Schwinger type of tensor forces. Here a component with given total angular momentum $J$ contains 3 orbital waves $L = J$, $J \pm 1$, the radial solutions of the two latter being coupled together by equations of the form:

$$\frac{d^2u_{J-1}}{dr^2} + \left[k^2 - w_1(r) - \frac{J(J-1)}{r^2}\right] u_{J-1} = w_2(r)\, u_{J+1} \quad (8)$$

$$\frac{d^2u_{J+1}}{dr^2} + \left[k^2 - w_3(r) - \frac{(J+1)(J+2)}{r^2}\right] u_{J+1} = w_2(r)\, u_{J-1}, \quad (9)$$

where $w_1(r)$, $w_2(r)$ and $w_3(r)$ are known functions of the radial factors of the central and non-central potentials and have the dimension of energy multiplied by $\mu/\hbar^2$.

For the solution to represent the scattering of an incident plane wave, the $u$-functions must have the asymptotic forms:

$$u_{J-1} \sim A_{J-1} \frac{1}{r} e^{i\eta_{J-1}} \sin\left[kr - (J-1)\pi/2 + \eta_{J-1}\right]$$

$$u_{J+1} \sim A_{J+1} \frac{1}{r} e^{i\eta_{J+1}} \sin\left[kr - (J+1)\pi/2 + \eta_{J+1}\right], \quad (10)$$

where $A_{J-1}$, $A_{J+1}$ are certain known constants.

In order to apply the perturbation method, one formally reduces the coupled equations to a pair of independent homogeneous equations by

writing the right-hand-side expressions of (8) and (9) respectively as

$$\left(w_2(r)\frac{u_{J+1}}{u_{J-1}}\right)u_{J+1} \text{ and } \left(w_2\frac{u_{J-1}}{u_{J+1}}\right)u_{J+1};$$

thus $u_{J-1}$, $u_{J+1}$ become virtually solutions for the radial potentials:

$$-w_1(r) - w_2(r)\frac{u_{J+1}}{u_{J-1}} \text{ and } -w_3(r) - w_2(r)\frac{u_{J-1}}{u_{J+1}}.$$

Let us regard $w_1(r)$, $w_2(r)$ and $w_3(r)$ as quantities of the first order for the perturbation calculation and make the corresponding series developments of $u_{J-1}$ and $u_{J+1}$. The above defined virtual potentials can be expressed as similar series containing terms of all orders. Although these potentials contain the unknown $u$-functions, for the perturbation calculation they are effectively as though given. For, to the $n$th order, the virtual potentials contain only $u$-functions to the $n-1$th order. Thus when the $n$th order terms in the potentials are required, they can already be calculated explicitly from the solutions of the previous stage. Consider, for instance, the stage of the calculation when the virtual potentials are known to the $n$th order. The phase shifts $\eta_{J-1}^{(n)}$, $\eta_{J+1}^{(n)}$ of the $n$th order and the corresponding wave functions of the closed states can be determined with the perturbation method as in the case of the central forces. The proper $u$-functions to the same order are obtained by normalizing the wave functions in accordance with the requirements (10). From the $n$th order $u$-functions the $n+1$th order terms in the virtual potentials can be calculated, hence the perturbation calculation can proceed one stage further. Following this procedure the first order phase shifts can be written down as readily as in the case of central forces and are found to be identical with the corresponding expressions given by Ashkin and Wu (1948) using Born's approximation. The second order corrections can be described as follows:—

Let

$$\eta_{(ab)}^{(2)} = 2\pi^2(-1)^a\Big[\int_0^\infty J_{(a+\frac{1}{2})}(kr')\,H_a(r')\,J_{-(a+\frac{1}{2})}(kr')\,r'dr' \times \times \int_0^{r'} J^2_{(a+\frac{1}{2})}(kr)\,H_a(r)\,rdr + \frac{A_b}{A_a}e^{i(\eta_b^{(1)}-\eta_a^{(1)})}\int_0^\infty (I_b J_{(a+\frac{1}{2})}(kr) - I_a J_{(b+\frac{1}{2})}(kr))\,rw_2(r)\,dr\Big], \quad (11)$$

where

$$H_a(r) = w_1(r) + \frac{A_b}{A_a}\frac{J_{(b+\frac{1}{2})}(kr)}{J_{(a+\frac{1}{2})}(kr)},\ H_b(r) = w_3(r) + \frac{A_a}{A_b}\frac{J_{(a+\frac{1}{2})}(kr)}{J_{(b+\frac{1}{2})}(kr)} \quad (12)$$

and

$$I_a = \tfrac{1}{2}\Big[ J_{(a+\frac{1}{2})}(kr) \int_0^r H_a(r') J_{(a+\frac{1}{2})}{}^{3}(kr')\, r'dr' + J_{(a+\frac{1}{2})}(kr) \times$$

$$\times \int_r^\infty H_a(r') J_{(a+\frac{1}{2})}(kr') J_{-(a+\frac{1}{2})}(kr')\, r'dr' \qquad (13)$$

$I_b$ being the same as $I_a$ with $a$ everywhere replaced by $b$. Then $\eta_{J-1}$ and $\eta_{J+1}$ are given by putting in (11) $a = J - 1$, $b = J + 1$ and $a = J + 1$, $b = J - 1$ respectively. The terms containing $I_a$ and $I_b$ are due to the first order corrections to the wave functions. It may be noticed here, that though the first order phase shifts (Born's approximation) are real, the second order expressions are complex quantities, thus giving complex phase-shifts, as is actually the case (see for example, Ashkin and Wu, 1948).

As far as we know the expression for second order corrections to the phase-shifts for non-central interactions have not been given before.

## SUMMARY

It is shown that the calculation of the phase-shifts can be reduced to an ordinary eigen-value problem (for a closed state). By applying the usual perturbation theory to the latter, one obtains readily the phase shifts as series in powers of the interaction potential. The procedure, it is shown, is applicable to non-central as well as centrally symmetric interactions. Explicit expressions for phase shifts upto second order are given for both kinds of potentials.

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# TSCHEBYSCHEFF POLYNOMIALS $T_n(z)$ AND $U_n(z)$ AND FUNCTIONS OF THE SECOND KIND

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Received August 24, 1951
(Communicated by Prof. B. S. Madhava Rao, F.A.SC.)

1. The Tschebyscheff polynomials $T_n(z)$ and $U_n(z)$ are special acess of the Jacobi polynomials $P_n^{(\alpha,\beta)}(z)$. The Jacobi function of the second kind denoted by $Q_n^{(\alpha,\beta)}(z)$ is introduced in the literature as a linearly independent second solution of the second order differential equation satisfied by $P_n^{(\alpha,\beta)}(z)$; and both $P_n^{(\alpha,\beta)}(z)$ and $Q_n^{(\alpha,\beta)}(z)$ satisfy the same recursion formula. Their inter-relations, and their various integral representations as well as representations by means of hypergeometric functions are wellknown [1]. In the important ultraspherical case ($\alpha = \beta$)—especially in the Legendre case ($\alpha = \beta = 0$)—these relations and formulæ are again explicitly set forth in [1]. The object of the present note is to point out the further simplifications that arise in the Tscheslybcheff cases ($\alpha = \beta = -\frac{1}{2}$ and $\alpha = \beta = +\frac{1}{2}$), our main result being that the Tschebyscheff functions of the second kind which we have denoted by $\bar{T}_n(z)$ and $\bar{U}_n(z)$ can be evaluated in very simple closed form. An attempt in this direction has recently been made by Bagchi and Chakravarty[2], who consider the difference and the differential equations satisfied by $T_n(z)$ and set out to write down their general solutions. But in the light of our introductory remarks, most of their results have turned out to be only particular cases of well-known results concerning the ultraspherical polynomials. In this context, our present note is intended as a postscript to the paper by Bagchi and Chakravarty[2].

2. With the notation of [1], the Tschebyscheff polynomials $T_n(z)$ and $U_n(z)$ are two particular solutions of the difference equation

$$f_{n+1}(z) - 2zf_n(z) + f_{n-1}(z) = 0, \quad (n \geq 1;\ f_0, f_1 \text{ arbitrary}). \tag{1}$$

The general solution of (1) is easily found to be

$$f_n(z) = A(z) \cdot (z + \sqrt{z^2-1})^n + B(z) \cdot (z - \sqrt{z^2-1})^n, \tag{2}$$

with

$$A(z) = \frac{f_1(z) - (z - \sqrt{z^2-1}) f_0(z)}{2\sqrt{z^2-1}},\ B(z) = \frac{(z + \sqrt{z^2-1}) f_0(z) - f_1(z)}{2\sqrt{z^2-1}}.$$

Again it can be easily seen that, between any two solutions $f_n(z)$ and $\bar{f}_n(z)$ of (1), the following relation holds:

$$f_n(z)\bar{f}_{n-1}(z) - f_{n-1}(z)f_n(z) = f_1(z)\bar{f}_0(z) - f_0(z)\bar{f}_1(z). \quad (3)$$

With the above considerations, we first introduce $T_n(z)$ and $\bar{T}_n(z)$ as two particular solutions of (1) as follows:

I. Take $f_0(z) = 1$, $f_1(z) = z$ and denote the polynomials $f_n(z)$ so determined by $T_n(z)$; thus

$$T_n(z) = \frac{(z + \sqrt{z^2-1})^n + (z - \sqrt{z^2-1})^n}{2}. \quad (4)$$

This is *Tschebyscheff's polynomial of the first kind*, or briefly, *Tschebyscheff's T-polynomial.*

I. Take $f_0(z) = 1$, $f_1(z) = z - \sqrt{z^2-1}$ and denote the $f_n(z)$ so determined by $\bar{T}_n(z)$; thus

$$\bar{T}_n(z) = (z - \sqrt{z^2-1})^n. \quad (5)$$

We shall call this *Tschebyscheff's T-function of the second kind.* As a particular case of (3), we note the following relation between $T_n(z)$ and $\bar{T}_n(z)$:

$$T_n(z)\bar{T}_{n-1}(z) - T_{n-1}(z)\bar{T}_n(z) = \sqrt{z^2-1}. \quad (A)$$

It is easy to verify that $T_n(z)$ and $\bar{T}_n(z)$ are two particular solutions of the differential equation

$$(1 - z^2)\frac{d^2w}{dz^2} - z\frac{dw}{dz} + n^2w = 0. \quad (6)$$

We now proceed to consider the standard solutions of this differential equation by the use of hypergeometric functions. We shall simply quote the results derived for $\lambda = 0$ from the ultraspherical case [1]: There is a polynomial solution of (6) given by [*cf.* 1, p. 84]

$$w = \begin{cases} (-1)^{\frac{n}{2}} F\left(-\frac{n}{2}, \frac{n}{2}; \frac{1}{2}; z^2\right), & n \text{ even}, \\ (-1)^{\frac{n-1}{2}}\, nz\, F\left(-\frac{n-1}{2}, \frac{n+1}{2}; \frac{3}{2}; z^2\right), & n \text{ odd}. \end{cases} \quad (7)$$

Also this satisfies the recursion (1) and evidently coincides with $T_n(z)$ for $n = 0, 1$; hence it is identical with $T_n(z)$. It is also the only polynomial solution of (6).

There is a second solution (proceeding purely according to negative powers of $z$) linearly independent of $T_n(z)$ and also satisfying the recursion (1) [*cf.* **1**, p. 85], *viz.*,

$$w = \frac{1}{2^n z^n} F\left(\frac{n}{2}, \frac{n+1}{2}; n+1; z^{-2}\right), \qquad (|z| > 1) \quad (8)$$

Denoting this provisionally by $T_n^*(z)$, we have

$$T_0^*(z) = 1 \equiv \bar{T}_0(z);$$

$$T_1^*(z) = \frac{1}{2z} F(\tfrac{1}{2}, 1; 2; z^{-2}) \qquad (|z| > 1)$$

$$= \tfrac{1}{2} z^{-1}\left[1 + \frac{1}{4} z^{-2} + \frac{1 \cdot 3}{4 \cdot 6} z^{-4} + \ldots\right]$$

$$= z - z\left[1 + \frac{-1}{2} z^{-2} + \frac{-1 \cdot 1}{2 \cdot 4} z^{-4} + \frac{-1 \cdot 1 \cdot 3}{2 \cdot 4 \cdot 6} z^{-6} + \ldots\right]$$

$$= z - z(1 - z^{-2})^{\frac{1}{2}} \equiv \bar{T}_1(z).$$

This identifies $T_n^*(z)$ with $\bar{T}_n(z)$ for all $n$, $(|z| > 1)$.

On the same lines as before, we next introduce $U_n(z)$ and $\bar{U}_n(z)$ as two other particular solutions of (1) as follows:

II. Take $f_0(z) = 1$, $f_1(z) = 2z$ and denote the polynomials $f_n(z)$ so determined by $U_n(z)$; thus

$$U_n(z) = \frac{(z + \sqrt{z^2-1})^{n+1} - (z - \sqrt{z^2-1})^{n+1}}{2\sqrt{z^2-1}}. \qquad (9)$$

This is *Tschebyscheff's polynomial of the second kind*, or briefly, *Tschebyscheff's U-polynomial*.

$\bar{\text{II}}$. Take $f_0(z) = \dfrac{z - \sqrt{z^2-1}}{\sqrt{z^2-1}}$, $f_1(z) = \dfrac{(z - \sqrt{z^2-1})^2}{\sqrt{z^2-1}}$ and denote the $f_n(z)$ so determined by $\bar{U}_n(z)$; thus

$$\bar{U}_n(z) = \frac{(z - \sqrt{z^2-1})^{n+1}}{\sqrt{z^2-1}}. \qquad (10)$$

We shall call this *Tschebyscheff's U-function of the second kind.* As a particular case of (3), we note the following relation between $U_n(z)$ and $\bar{U}_n(z)$:

$$U_n(z)\,\bar{U}_{n-1}(z) - U_{n-1}(z)\,\bar{U}_n(z) = \frac{1}{\sqrt{z^2-1}}. \qquad (B)$$

It is easy to verify that $U_n(z)$ and $\bar{U}_n(z)$ are two particular solutions of the differential equation

$$(1 - z^2)\frac{d^2w}{dz^2} - 3z\frac{dw}{dz} + n(n+2)w = 0. \tag{11}$$

We now proceed to consider the standard solutions of this differential equation by the use of hypergeometric functions. As before, we shall only quote the results derived for $\lambda = 1$ from the ultraspherical case [1]:

There is a polynomial solution of (11) given by [*cf.* **1**, p. 84]:—

$$w = \begin{cases} (-1)^{\frac{n}{2}} F\left(-\frac{n}{2}, \frac{n}{2}+1; \frac{1}{2}; z^2\right), & n \text{ even}, \\ (-1)^{\frac{n-1}{2}} (n+1)\, z\, F\left(-\frac{n-1}{2}, \frac{n+1}{2}+1; \frac{3}{2}; z^2\right), & n \text{ odd}. \end{cases} \tag{12}$$

Also this satisfies the recursion (1) and evidently coincides with $U_n(z)$ for $n = 0, 1$; hence it is identical with $U_n(z)$. It is also the only polynomial solution of (11).

There is a second solution (proceeding purely according to negative powers of $z$) linearly independent of $U_n(z)$ and also satisfying the recursion (1) [*cf.* **1**, p. 85], *viz.*,

$$w = \frac{1}{2^{n+1} z^{n+2}} F\left(\frac{n}{2}+1, \frac{n+1}{2}+1; n+2; z^{-2}\right), \quad (|z| > 1) \tag{13}$$

Denoting this provisionally by $U_n^*(z)$, term-by-term differentiation of the corresponding series for $T_{n+1}^*(z)$ w. r. t. z (which is justifiable) gives at once

$$U_n^*(z) = -\frac{1}{n+1} T_{n+1}^{*\prime}(z).$$

Since we have already identified $T_n^*(z)$ with $\bar{T}_n(z)$, this immediately identifies $U_n^*(z)$ with $\bar{U}_n(z)$, $\quad (|z| > 1)$.

Finally, in addition to the two relations (A) and (B), which are analogous to a well-known relation between the Legendre functions $P_n(z)$ and $Q_n(z)$, we note that

$$\bar{T}_n(z) = \sqrt{z^2-1}\, \bar{U}_{n-1}(z), \; \bar{U}_n(z) = \frac{1}{\sqrt{z^2-1}} \bar{T}_{n+1}(z). \tag{C}$$

We conclude this note by mentioning one of the various integral representations of our functions readily derivable for $\lambda = 0$ and $\lambda = 1$ from the ultraspherical case [*cf.* **1**; pp. 82, 85]:

$$\int_{-1}^{+1} \frac{T_n(t)}{\sqrt{1-t^2}} \frac{dt}{z-t} = \frac{n!}{(2n-1)!!} \int_{-1}^{+1} (1-t^2)^{n-\frac{1}{2}} \frac{dt}{(z-t)^{n+1}} = \pi \bar{U}_{n-1}(z)$$

$$= \pi \frac{\bar{T}_n(z)}{\sqrt{z^2-1}}, \qquad (|z| > 1); \qquad (14)$$

$$\int_{-1}^{+1} \sqrt{1-t^2}\, U_n(t) \frac{dt}{z-t} = \frac{(n+1)!}{(2n+1)!!} \int_{-1}^{+1} (1-t^2)^{n+\frac{1}{2}} \frac{dt}{(z-t)^{n+1}} = \pi \bar{T}_{n+1}(z)$$

$$= \pi \sqrt{z^2-1}\, \bar{U}_n(z), \quad (|z| > 1). \qquad (15)$$

Incidentally we have obtained here the evaluations, in finite terms, of four interesting definite integrals.

One of us (T. S. N.) wishes to thank the Government of India for the award of a Senior Research Scholarship and Prof. B. S. Madhava Rao for kind encouragement.

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# ON THE DISTRIBUTION OF THE RANGE OF VARIATION OF THE ORDERED VARIATES IN SAMPLES OF $n$ FROM NORMAL UNIVERSE

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Received August 20, 1951

(Communicated by Prof. B. S. Madhava Rao, F.A.Sc.)

McKay (1935) and others have found the distribution of the extreme deviate from the sample mean of ordered variates.

Here I shall consider the distribution of the range of variation of $n$ ordered variates, *i.e.*, the distance between the extremes and also the deviation of the sample mean from the mean of the extreme variates.

Let $x_1, x_2, \ldots, x_n$ be ordered variates drawn from a parent universe which is normal with origin as the mean and standard deviation $\sigma$. Then the joint distribution of the ordered variates $x_1, x_2, \ldots, x_n$ is

$$\frac{\lfloor n}{\sigma^n [\sqrt{2\pi}]^n} \exp. \left[ - \frac{1}{2\sigma^2} \sum_1^n x_i^2 \right] \pi dx_i$$

Let $T_i = \frac{1}{\sqrt{i(i+1)}} [(x_n + \ldots + x_{n-1+1}) - ix_n - i]$

$= \frac{z_i}{\sqrt{i(i+1)}}$ $(i = 1, 2, \ldots n-1)$ and $y_n = \frac{1}{\sqrt{n}} \sum_{i=1}^n x_i$

$= \sqrt{n}\, \bar{x}$. Then $\sum_1^n x_i^2 = \sum_1^n y_i^2 = \sum_1^{n-1} \frac{z_i^2}{i(i+1)} + n\bar{x}^2$

$$\prod_{i=1}^n dx_i = \prod_{i=1}^n dy_i = \frac{1}{\lfloor n-1} \, d\bar{x} \prod_{i=1}^{n-1} dz_i.$$

The joint distribution of $\bar{x}, z_1, z_2, \ldots z_{n-1}$ will be

$$\frac{\lfloor n}{\sigma^n [\sqrt{2\pi}]^n} \exp. \left[ - \frac{n\bar{x}^2}{2\sigma^2} - \frac{1}{2} \sum_1^{n-1} \frac{z_i^2}{2\sigma^2 i(i+1)} \right] d\bar{x} \cdot \prod_{i=1}^{n-1} dz_i$$

Integrating with respect to $x$ from $-\alpha$ to $\alpha$ we have the joint distribution of $z_1, z_2, \ldots, z_{n-1}$ as

$$\frac{\sqrt{n}}{\sigma^{n-1} [\sqrt{2\pi}]^{n-1}} \exp. \left[ - \frac{1}{2} \sum_{i=1}^{n-1} \frac{z_i^2}{2\sigma^2 i(i+1)} \right] \prod_{i=1}^{n-1} dz_i$$

Now $0 \leqslant z_1 \leqslant z_i \ldots . \leqslant z_{n-1} = n(\bar{x} - x_1) = n\bar{u}$ (2)

Let $B_0(x) = 1,\ B_r(x) = \int_0^x \exp.\left[\frac{-t^2}{2\sigma^2 r(r+1)}\right] B_{r-1}(t)\, dt.$

Then $B_r(x) = \sigma^r G_r\left(\frac{x}{\sigma}\right)$, where G-functions defined by Godwin (1945) are as follows:—

$$G_0(x) = 1,\ G_r(x) = \int_0^x \exp.\left[\frac{-t^2}{2r(r+1)}\right] G_{r-1}(t)\, dt.$$

Integrating (1) with respect to $z_1, z_2, \ldots . z_{n-1}$, between the limits (2) we have the distribution of $u$ as

$$f_n(n)\, du = \frac{n\sqrt{n}\, du}{\sigma^{n-1}[\sqrt{2\pi}]^{n-1}} \exp.\left[\frac{-nu^2}{2\sigma^2(n-1)}\right] B_{n-2}(nu)$$

Let $v = x_n - \bar{x}$ and putting $y_i = \frac{1}{\sqrt{i(i+1)}}\{ix_{i+1} - (x_i + \ldots . + x_1)\}$

$i = 1, 2, \ldots . n-1$

as before we have the distribution of $v$ as

$$f_n(v)\, dv = \frac{n\sqrt{n}\, dv}{\sigma^{n-1}[\sqrt{2\pi}]^{n-1}} \exp.\left[\frac{-nv^2}{2\sigma^2(n-1)}\right] B_{n-2}(nn)$$

Hence the joint distribution of $u$, $v$ will be

$$\frac{n^2(|n)^2\, du dv}{\sigma^{2n-2}[2\pi]^{n-1}} \exp.\left[-\frac{n(n^2+v^2)}{2\sigma^2(n-1)}\right] B_{n-2}(nu)\, B_{n-2}(nv)$$

Let $u + v = t$, $u - v = s$. Then $t = x_n - x_1 =$ range of variation.

$\frac{s}{2} = \frac{x_n + x_1}{2} - \bar{x} =$ deviation of the mean of the variates from the mean of the extreme values.

$u = \frac{t+s}{2}$, $v = \frac{t-s}{2}$. Therefore $\left|\frac{\partial(u, v)}{\sigma(t, s)}\right| = \frac{1}{2}$

$-a \leqslant s \leqslant a,\ 0 < t \leqslant a.$

Hence the distribution of the range of variation, *i.e.*, $t$ is

$$\frac{n^2(|n)^2}{\sigma^{2n-2}[2\pi]^{n-1}} \cdot \exp.\left[\frac{-nt^2}{4\sigma^2(n-1)}\right] \int_0^a \exp.\left[\frac{-ns^2}{4\sigma^2(n-1)}\right] B_{n-2}\left\{\frac{n(t+s)}{2}\right\} \times$$

$$\times\, B_{n-2}\left\{\frac{n(t-s)}{2}\right\} ds$$

The distribution of $s$ will be

$$\frac{n^2(\lfloor n\, n)^2}{2\sigma^{2n-2}(2\pi)^{n-1}} \exp.\left[-\frac{ns^2}{4\sigma^2(n-1)}\right] \int_0^a \exp.\left[-\frac{nt^2}{4\sigma^2(n-1)}\right] \times$$

$$B_{n-2}\left\{\frac{n(t+s)}{2}\right\} B_{n-2}\left\{\frac{(t-s)n}{2}\right\} dt.$$

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# EFFECT OF SURFACE ACTIVE SUBSTANCES ON THE CAPACITY OF THE ELECTRIC DOUBLE LAYER

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Received November 16, 1951

## Introduction

While studying the effect of surface active substances on the kinetics of discharge of cadmium ion at the dropping mercury electrode in pulsating fields[1] it was observed that the velocity of discharge was greatly brought down by the presence of such substances as gelatin. Randles[2] has used an elegant technique based on measurement of phase difference and has reported that the rate of discharge of cadmium ions is brought down a thousand-fold by the addition of gelatine. Similar results have been reported by Keilin[3] who has found that the limiting current in polarography is lowered markedly by the presence of surface active substances; this has been attributed to the surface active substance getting adsorbed at the mercury surface and preventing electrode processes in the covered areas. The adsorption of surface active substances is known to lower the capacity of the electric double layer and is often responsible for low values of the capacity reported in literature.[4] The present work relates to a detailed study of the effect of adsorption of a few surface active substances on the capacity of the electric double layer at the dropping mercury electrode.

## Experimental

A simple technique for getting an idea of the capacity of the electric double layer is afforded by the Breyer-Gutman technique[5] based on the measurement of A.C. current produced by subjecting the dropping mercury electrode to pulsating fields. The technique consists in applying simultaneously a D.C. potential by the potentiometer $P_1$ (Fig. 1) and an A.C. ripple by the potentiometer $P_2$ and measure the A.C. component of the pulsating current produced, by measuring the A.C. potential drop across the resistance R. The details have been described previously.[6,7]

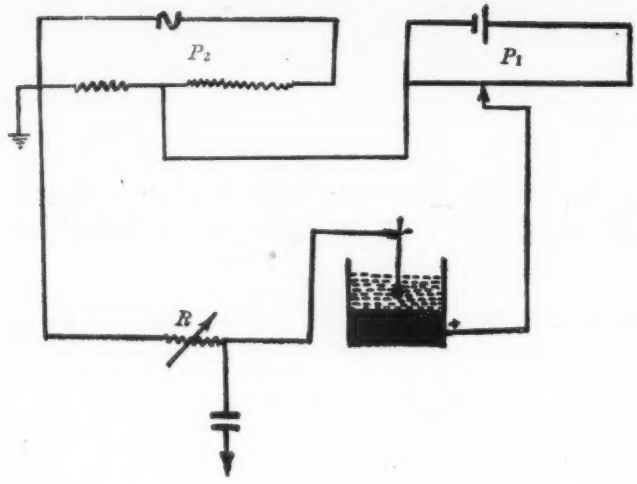
$P_2$
$P_1$
R

FIG. 1

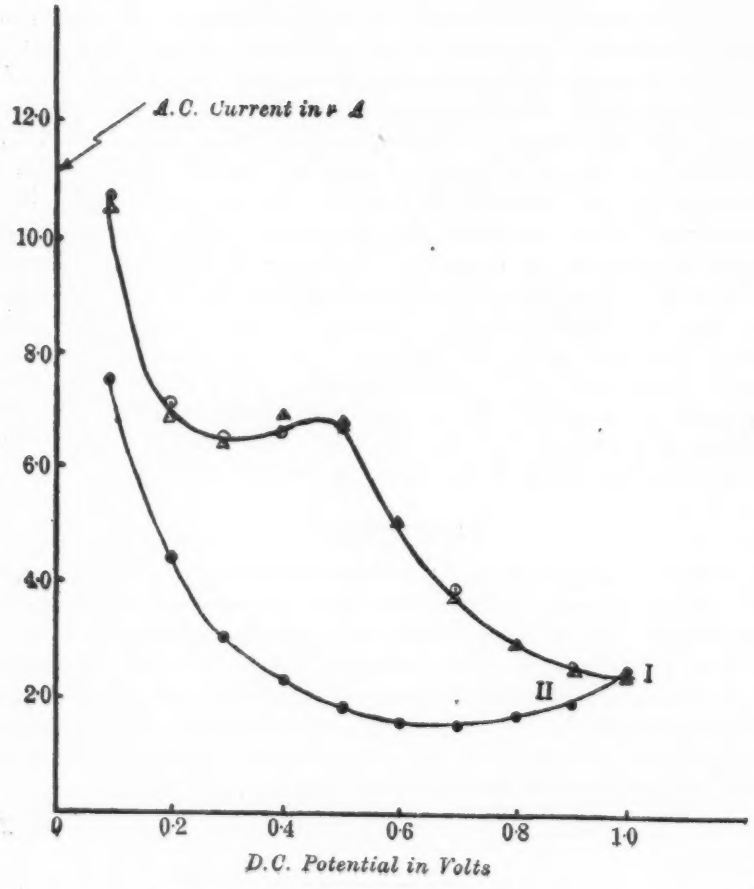
A.C. Current in μ A
12·0
10·0
8·0
6·0
4·0
2·0
0
0·2
0·4
0·6
0·8
1·0
I
II
D.C. Potential in Volts

FIG. 2

The magnitude of the alternating current is directly a measure of the capacity of the electric double layer. Curve 1 in Fig. 2 gives the A.C. current–D.C. potential curve for one molar potassium chloride which is freed from air by bubbling hydrogen. Measurements are also taken with molar potassium chloride solution containing dissolved air; but the A.C. current values are found to be identical whether oxygen is present or not, as can be seen from Fig. 2. Hence the rest of the experiments are carried out without removal of air. Curve 2 represents the effect of surface active substances present in sugarcane juice at different D.C. potentials. An examination of the curve shows that the effect of surface active substances on the capacity of the electric double layer is maximum in the neighbourhood of an applied potential of 0·5 V which is near the electrocapillary zero. Similar observations have been made by Frumkin[8] in his study of the effect of picein on the double layer capacity. Adsorption of pyridine also shows a similar feature. Later measurements are therefore limited to the effect produced at a D.C. potential of 0·5 V applied through the mercury pool. The effect of different concentrations of acetone, thymol blue, isobutyl alcohol and gelatin on the A.C. current developed, is given in Tables I to IV. Table V gives the effect of addition of sparingly soluble organic substances on the double layer capacity.

TABLE I

*Acetone*

| Volume in c.c. added to 30 c.c. of molar KCl | A.C. Current in/μ A | Drop-time in sec. |
|---|---|---|
| 0 | 6·97 | 5·1 |
| 0·2 | 6·65 | 5·08 |
| 0·4 | 6·22 | .. |
| 0·8 | 5·27 | .. |
| 1·0 | 4·89 | .. |
| 1·2 | 4·42 | 5·06 |
| 1·4 | 3·99 | .. |
| 1·6 | 3·66 | 5·02 |
| 1·8 | 3·40 | .. |
| 2·0 | 3·20 | 4·98 |
| 3·0 | 2·42 | 4·9 |
| 4·0 | 2·15 | 4·86 |
| 5·0 | 2·00 | .. |
| 6·0 | 1·89 | 4·80 |
| 7·0 | 1·80 | 4·80 |
| 8·0 | 1·76 | .. |
| 10·0 | 1·68 | 4·74 |

TABLE II

*Thymol Blue* 0·04%

| Volume in c.c. added to 30 c.c. of molar KCl | A.C. Current in/μ A | Drop-time in sec. |
|---|---|---|
| 0 | 7·06 | 5·32 |
| 0·5 | 5·50 | 5·42 |
| 1·0 | 3·99 | 5·42 |
| 1·5 | 2·83 | 5·42 |
| 2·0 | 2·09 | 5·34 |
| 2·5 | 1·72 | 5·18 |
| 3·0 | 1·56 | 5·1 |
| 3·5 | 1·45 | 5·1 |
| 4·0 | 1·38 | 5·0 |
| 4·5 | 1·35 | 5·0 |
| 5·0 | 1·31 | 5·0 |
| 5·5 | 1·31 | 4·98 |

TABLE III

*Isobutyl Alcohol*

| Volume in c.c. added to 30 c.c. of molar KCl | A.C. Current in/μ A | Drop-time in sec. |
|---|---|---|
| 0 | 7·06 | 5·28 |
| 0·1 | 5·61 | 5·28 |
| 0·2 | 1·58 | 5·26 |
| 0·3 | 1·24 | 5·22 |
| 0·4 | 1·04 | 5·14 |
| 0·5 | 0·99 | 5·16 |
| 0·6 | 0·96 | .. |
| 0·8 | 0·94 | 5·10 |
| 0·9 | 0·91 | 5·04 |
| 1·0 | 0·91 | 5·04 |
| 1·2 | 0·88 | 5·02 |

TABLE IV

*Gelatin* 2%

| Volume in c c. added to 30 c.c. molar KCl | D.C. Current in/μA |
|---|---|
| 0 | 7·19 |
| 0·05 | 6·08 |
| 0·1 | 5·41 |
| 0·15 | 4·51 |
| 0·2 | 4·05 |
| 0·25 | 3·77 |
| 0·4 | 3·44 |
| 0·8 | 2·89 |
| 1·6 | 2·88 |
| 2·6 | 2·86 |

TABLE V

*Effect on Sparingly Soluble Organic Substances*

| Substance | % reduction in A. C. current |
|---|---|
| Benzene .. | 95·1 |
| Toluene .. | 89·0 |
| Amyl alcohol .. | 86·9 |
| Xylene .. | 73·1 |

## DISCUSSION

(1) *The effect of soluble surface active substances on the double layer capacity.*—The alternating current passing through the system depends upon (*a*) the capacity of the double layer and (*b*) the size of the drops. As seen from the tables, however, the drop time which is a measure of the size of the drop is not appreciably changing. From this it is clear that the A.C. current values are practically a measure of capacities of the electric double layer. That the A.C. current is mostly capacitative can be further confirmed from the fact that the magnitude of the current is practically directly proportional to the frequency of the A.C. current.[7]

It is found that as the concentration of the surface active substance increases, the double layer capacity diminishes in the first instance and finally attains a more or less constant value. The final low value obtained at high concentrations is different in different cases. The effect on the double layer capacity increases in the order: gelatine, acetone, thymol blue and isobutyl alcohol. These differences are partly due to the surface being covered to different extents at saturation and partly due to the differences in the double layer capacity of covered parts in the different cases. A quantitative formulation of these should await further accumulation of experimental data.

2. *Effect of sparingly soluble organic substances.*—The sparingly soluble substances have a profound effect in decreasing the double layer capacity. The effect in the decreasing order is with benzene, toluene, amyl alcohol and xylene. The large effect of benzene was at first feared to be due to the traces of thiophene. Accordingly the benzene was purified so as to get a sample not answering the test for thiophene. But the decrease in capacity remained nearly the same.

3. *Possible application.*—The observations made herein appear to be capable of application for the estimation of surface active substances. Amongst the other methods that are available are (*a*) determination of surface and interfacial tensions and (*b*) depression of polarographic maxima. The determination of surface tension or interfacial tension is attended by many difficulties and the correlation of the surface tension with the concentration of the surface active substance is often complicated. We may further point out that the interfacial tension between the mercury and the aqueous solution is only affected to a minor extent by the surface active substances examined herein and therefore would give no precise idea of the concentration. The method based on the polarographic maximum is open to criticism as the maximum is caused by the dynamic effects due to electrocapillaryphoresis[9] at the dropping mercury electrode. (The electrocapillaryphoresis is perhaps brought about due to the fresh mercury surface just formed near the capillary tip having a different interfacial tension from that of the old surface at the apex of the drop due to the deposition of the ion getting discharged. At higher potentials the discharge of the ion is very quick and takes place even at the fresh surface sufficiently quickly to render differences in interfacial tension negligible; hence the electrocapillary phoresis ceases; the current falls). Such maxima can hardly be expected to be reproducible sufficiently to give precise measure of the surface active substances. From these points of view, measurement of double layer capacity affords an advantage. The double layer capacity itself can be measured by a number of methods. The methods based on D.C. current are definitely disadvantageous as the capacity is greatly influenced by the presence of oxygen. The Breyer and Gutman technique, on the other hand, has a unique advantage in this regard, since the presence of air has practically no influence on the magnitude of the alternating current observed. This is due to the fact that the electrode process involving oxygen is slow and does not follow the pulsating fields even when the pulsation are as low as 50 cycles per second. Further since the mercury drop is freshly being formed, there is no complication due to external contamination. An alternative to this technique would be the method described by Grahame[10] using the bridge suitably modified, if necessary. The present method appears to be invaluable for control purposes wherever the elimination of surface active substances is to be followed up.

The authors wish to thank the Uttar Pradesh Scientific Research Committee for the grant which made this work possible, and Professor J. M. Saha, Director, Indian Institute of Sugar Technology, Kanpur, for his kind interest.

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# NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

## Part XXXV. Isomerisation of 5 : 7 : 8-Hydroxy Chromones into 5 : 6 : 7-Hydroxy Chromones

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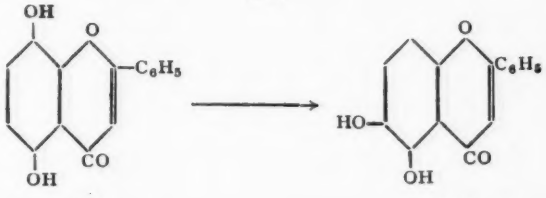
Received November 24, 1951

The methods of nuclear oxidation have been successfully employed for the synthesis of flavonols, flavones and their partial methyl ethers which are otherwise more difficult to obtain (*vide* previous parts). These convenient methods have not been used for the preparations in the simpler group of chromones. Derivatives of chromones with the 5:7:8 and 5:6:7 arrangement of the hydroxyl groups were needed in connection with the study of possible isomeric changes in the chromone group and the application of the methods of nuclear oxidation for their preparation is described in this paper.

In the case of wogonin (I *b*) and primetin (II) derivatives treatment with hydriodic acid was found to bring about change into the isomeric structures with 5:6:7 (III) and 5:6 (IV) orientation of hydroxyl groups.[1] The change was not noticed in the corresponding flavonol derivatives. From the results of experiments recorded with flavone derivatives it could be concluded that the change is rather slow and requires heating for at least two hours for completion. It seems to be also clear that isomers with the 5:6:7 arrangement of hydroxyl groups (III) are more stable than those having the alternative 5:7:8 arrangement (I *a*); the former tend to be produced exclusively after treatment of the latter with hydriodic acid and the reverse change does not seem to be appreciable. Consequently this provides a convenient method of preparing the flavones with the 5:6:7 orientation.[2] Though it is obvious that in this isomerisation the pyrone ring opens out and closes again using a different hydroxyl,[3] no clear mechanism has so far been suggested and no comprehensive investigation made on the influence of the substituent groups. It is one of the objects of the present work to provide the necessary data.

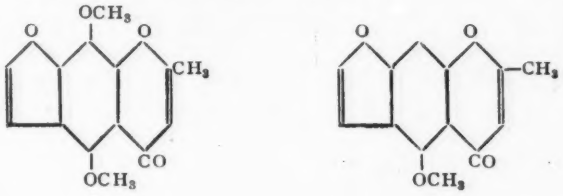
(I) (III)

(*a*) R=H
(*b*) R=$CH_3$



(II) (IV)

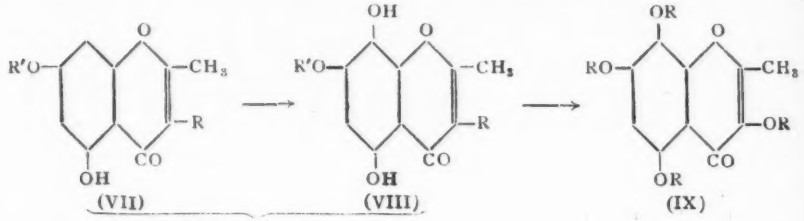
The above-mentioned isomerisation met with in the flavone series and the influence of the substituents in the 3-position have not so far been studied in the case of the simpler chromones. Apart from the question of the extension of the field of study a new interest has arisen by the observations of Robertson and co-workers who have recorded that in the case of kellin (V) and visnagin (VI) action of hydriodic acid involves isomerisation of the furan ring and not of the pyrone ring.[4]



(V) (VI)

5: 7-Dihydroxy-3-methoxy-2-methyl chromone (VII *a*) undergoes oxidation with alkaline persulphate to give a good yield of the corresponding 5: 7: 8-trihydroxy compound (VIII *a*). Oxidation of the 3: 7-dimethyl ether (VII *b*) is also found to proceed smoothly but the yield of the product is not better and hence there is no particular advantage in employing this partial methyl ether. Methylation of these compounds yields the 3: 5: 7: 8-tetramethyl ether (IX *a*) and demethylation gives rise to 3: 5: 7: 8-tetrahydroxy-2-methyl chromone (IX *b*). The properties of the demethylated product agree in every respect with the expectations for the 5: 7: 8 arrangement of hydroxyl groups. That there is no isomeric change during

this demethylation is confirmed by methylation of the tetrahydroxy compound whereby 3:5:7:8-tetramethyl ether identical with (IX *a*) is obtained.

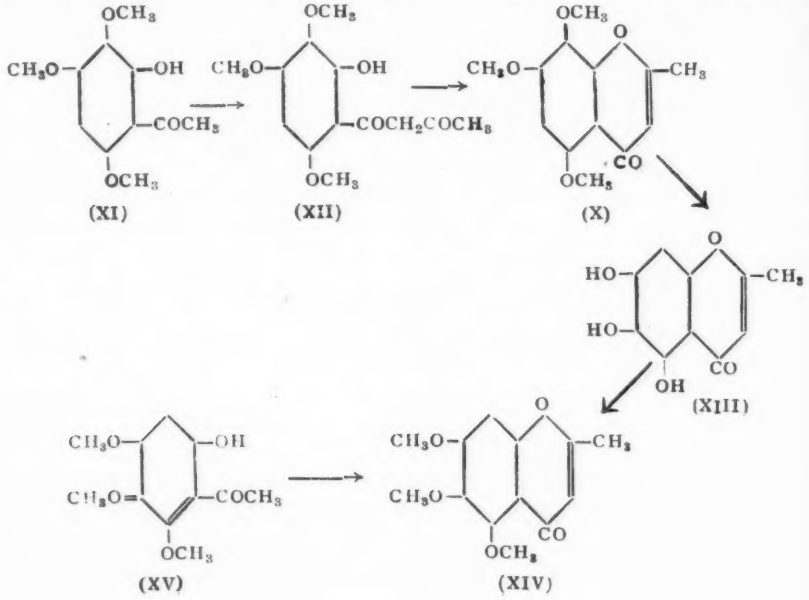


(VII) (VIII) (IX)

(*a*) R=$OCH_3$; R'=H
(*b*) R=$OCH_3$; R'=$CH_3$
(*c*) R=R'=H

(*a*) R=$CH_3$
(*b*) R=H

For the preparation of 5:7:8-trihydroxy-2-methyl chromone (VIII *c*) and its methyl ether, alkaline persulphate oxidation of the corresponding 5:7-dihydroxy compound (VII *c*) was first used but the yield of the product was not satisfactory. 5:7:8-Trimethoxy-2-methyl chromone (X) could, however, be prepared more easily starting from 2-hydroxy-3:4:6-trimethoxy acetophenone (XI). Of the methods examined for the chromone ring closure the most convenient one involves conversion of it into the corresponding diketone (XII) by condensation with ethyl acetate in the presence

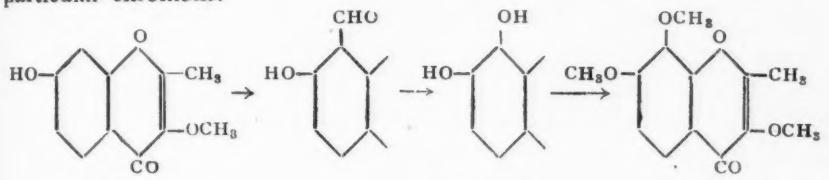


(XI) (XII) (X) (XIII) (XV) (XIV)

of sodium and subsequent closing up of the pyrone ring by means of alcoholic sulphuric acid. Demethylation of the trimethoxy chromone involves also isomeric change because the properties of the product are different from those of the 5:7:8-trihydroxy-2-methyl chromone (VIII *c*) prepared by direct nuclear oxidation but correspond with those expected for the 5:6:7 arrangement (XIII). This conclusion is also confirmed by the fact that the trimethyl ether obtained by remethylation of the demethylated product differs from 5:7:8-trimethoxy-2-methyl chromone (X). For purposes of confirmation the 5:6:7-trimethoxy-2-methyl chromone (XIV) has been synthesised by an unequivocal method starting from 2-hydroxy-4:5:6-trimethoxy acetophenone (XV)[5] and using the same method of chromone ring formation as described above.

It is thus clear that the isomeric change in the simpler chromones follows the same lines as in the case of the flavones and is obviously controlled by the same factors: chromonol derivatives (3-hydroxy) do not undergo the isomeric change whereas chromones without this substitution in the 3-position do. It may be mentioned here that for the preparation of the 5:6:7-trihydroxy-2-methyl chromone and its methyl ether the method involving isomerisation of the 5:7:8 isomer seems to be more convenient than the method of direct synthesis.

The two-stage process of nuclear oxidation[6] has now been applied to 7-hydroxy-3-methoxy-2-methyl chromone (XVI) and thereby the corresponding 7:8-dihydroxy-3-methoxy-2-methyl chromone (XVII) is obtained. Since there is no convenient method for preparing ω-methoxy gallacetophenone the above method is the only satisfactory one for the preparation of this particular chromone.




(XVI) (XVII) (XVIII)

## EXPERIMENTAL

### 5:7:8-*Trihydroxy-3-methoxy-2-methyl chromone* (*VIII a*)

5:7-Dihydroxy-3-methoxy-2-methyl chromone (1 g.) was dissolved in a solution of sodium hydroxide (0·75 g.) in water (15 c.c.). The brownish-red solution was mechanically stirred while keeping the flask in a water-bath at 10–15° C. and to it was added dropwise a saturated solution of

potassium persulphate (2 g.). During this addition the colour of the solution became deeper. After the addition was complete (3 hours) the contents were stirred for two hours more and then left overnight at room temperature. The solution was then made just acidic to congo red with concentrated hydrochloric acid and the unconverted chromone extracted with ether. The aqueous layer was made strongly acidic with concentrated hydrochloric acid (15 c.c.), sodium sulphite (about 4 g.) was added and the mixture heated in a boiling water-bath for 20 minutes to hydrolyse the intermediate sulphate. On cooling the solution in ice for an hour the trihydroxy compound separated as brown shining crystals. This was filtered and the mother-liquor repeatedly extracted with ether. On evaporating ether extract an yellowish-brown solid was obtained. This was combined with the product that was filtered off and crystallised from ethyl acetate-benzene mixture when the trihydroxy chromone was obtained as yellow rectangular needles which turn brown at 195° and melt with decomposition at 242–44°. The substance is sparingly soluble in ether and benzene but highly soluble in acetone, alcohol and ethyl acetate. Yield, 0·4 g. The recovery of the original chromone was 0·12 g. (Found: C, 48·4; H, 4·8; $C_{11}H_{11}O_6$, $2H_2O$ requires C, 48·2; H, 5·1).

The compound gives a green colour with ferric chloride in alcoholic solution which changes to brown with excess. It does not dissolve in cold aqueous sodium bicarbonate solution; on warming it dissolves to a pink solution which changes to yellow on boiling. With aqueous sodium carbonate a bright yellow solution is obtained which becomes colourless on shaking with air. It dissolves in aqueous sodium hydroxide to a brownish-yellow solution which quickly fades and then turns violet. With benzoquinone in alcohol the compound develops a very pale brown colour. It does not answer Bargellini's test.

3 : 7-*Dimethoxy-5-hydroxy-2-methyl chromone* (*VII b*)

5 : 7-Dihydroxy-3-methoxy-2-methyl chromone (1 g.) was dissolved in dry acetone (35 c.c.), dimethyl sulphate (0·5 c.c.) and freshly ignited potassium carbonate (3 g.) were added and the mixture gently refluxed on a water-bath for 6 hours. The acetone solution was then filtered and the inorganic salts repeatedly washed with hot acetone. The solvent was distilled off and the residue on cooling solidified to a colourless crystalline mass. The dimethyl ether was crystallised from benzene when it was obtained as stout rhombohedral prisms melting at 121–22°. Yield, 0·8 g. (Found: C, 61·5; H, 5·0; $C_{12}H_{12}O_5$ requires C, 61·0; H, 5·1).

The compound is sparingly soluble in alcohol and the solution shows a faint green fluorescence. It gives a purple colour with alcoholic ferric chloride.

3:7-*Dimethoxy*-5:8-*dihydroxy*-2-*methyl chromone* (*VIII b*)

The above partial methyl ether (1 g.) was dissolved in redistilled pyridine (5 c.c.) and to the brown solution was added aqueous sodium hydroxide (0·75 g. in 10 c.c. of water) when the pale yellow sodium salt separated out. A little more pyridine (3 c.c.) was added when the sodium salt partly dissolved. The resulting mixture had a pale yellow colour with faint greenish fluorescence. To this suspension which was mechanically stirred and maintained at 10–15° C. by immersing the flask in an ice-water-bath, was added dropwise a saturated aqueous solution of potassium persulphate (2 g. in 35 c.c.). During the addition, which took about 5 hours, the solid gradually went into solution and the colour of the solution changed to pale brown. The stirring was continued for two hours more by which time the whole of the sodium salt dissolved, and the contents were left overnight at room temperature. Next day the solution was found to have acquired a deep brown colour; it was made just acidic to congo red with strong hydrochloric acid and the unreacted original compound (0·1 g.) recovered by ether extraction. The aqueous solution was made strongly acidic with concentrated hydrochloric acid (15 c.c.), sodium sulphite (3–4 g.) was added and the solution heated on a boiling water-bath for 20 minutes. After cooling, it was thoroughly extracted with ether, the extract concentrated and the lemon-yellow solid crystallised from benzene-acetone mixture when the quinol was obtained as stout golden yellow prisms turning brown at 190° and melting at 216–18° (decomp.). Yield, 0·4 g. (Found: C, 57·4; H, 5·2; $C_{12}H_{12}O_6$ requires C, 57·2; H, 4·8).

The compound gives a deep green colour with alcoholic ferric chloride which deepens with excess and changes overnight to deep brown. It dissolves immediately in aqueous sodium hydroxide to a deep yellow solution which on shaking with air turns rose-red, then purple and soon assumes a violet tinge; the colour slowly fades off. *p*-Benzoquinone produces a pale brown colour with an alcoholic solution of the substance.

3:5:7:8-*Tetramethoxy*-2-*methyl chromone* (*IX a*)

5:7:8-Trihydroxy-3-methoxy-2-methyl chromone (0·23 g.) was dissolved in dry acetone (25 c.c.), redistilled dimethyl sulphate (0·3 c.c.) and freshly ignited potassium carbonate (3 g.) were added and the mixture gently refluxed for 30 hours. The product was worked up as usual and the com-

pound crystallised from water containing a few drops of alcohol when it was obtained as colourless fine needles melting at 158–9° (Found: C, 53·7; H, 6·1; $C_{14}H_{16}O_6$, $2H_2O$ requires C, 53·2; H, 6·3).

*Demethylation of* 5: 7: 8-*trihydroxy*-3-*methoxy*-2-*methyl chromone to* (*IX b*)

The trihydroxy chromone (1·3 g.) was dissolved in acetic anhydride (2. c.c.) by warming and to the solution was added hydriodic acid (15 c.c., d. 1·7) carefully in small quantities with cooling. The clear dark red solution was refluxed for 2 hours in an oil-bath at 140–50°. The mixture was diluted with a large quantity of a saturated solution of sodium bisulphite and left overnight. As only a small quantity of an yellow solid separated, the mixture was diluted with more water and thoroughly extracted with ether. On distilling off the solvent and removing acetic acid under reduced pressure a brownish-yellow solid was left behind. It crystallised from acetone-benzene mixture as yellow small prisms turning brown at 250° and decomposing at 270–73°. Yield, 0·63 g. (Found: C, 53·0; H, 4·0; $C_{10}H_8O_6$ requires C, 53·6; H, 3·6).

With alcoholic ferric chloride the compound gives a transient green colour which changes to brown. The colour deepens on addition of excess of the reagent. The substance slowly dissolves in sodium bicarbonate solution with a pink colour which on shaking turns rose-red, purple, violet and deep rose-red in quick succession. The colour gradually fades in two hours and completely disappears in 24 hours. In aqueous sodium carbonate and hydroxide purple solutions are obtained which quickly turn violet on shaking with air; the colour fades off overnight. *p*-Benzoquinone produces a brownish colour with an alcoholic solution of the compound; the solution slowly turns yellow which fades away. With sodium amalgam in absolute alcohol an immediate purple colour is produced which gradually changes to violet. In 2 hours the solution becomes colourless and a small quantity of a purple precipitate settles down.

*Remethylation to* (*IX a*)

The tetrahydroxy chromone (0·45 g.) was methylated in dry acetone solution with redistilled dimethyl sulphate (0·82 c.c.) in the presence of anhydrous potassium carbonate (5 g.) by refluxing for 32 hours. The tetramethyl ether was isolated as usual and crystallised from ethyl acetate-petroleum ether mixture. It was obtained as colourless fine needles melting at 157–8°. The mixed melting point with 3: 5: 7: 8-tetramethoxy-2-methyl chromone (IX *a*) prepared by direct methylation of (VIII *a*) was undepressed proving their identity.

7:8-*Dihydroxy*-3-*methoxy*-2-*methyl chromone* (*XVII*)

7-Hydroxy-3-methoxy-2-methyl chromone-8-aldehyde[7] (0·6 g.) was dissolved in aqueous sodium hydroxide (0·12 g. in 15 c.c. of water). To the bright yellow solution which was cooled in ice-water was added a solution of hydrogen peroxide (4·5 c.c. of 6% hydrogen peroxide diluted with 10 c.c. of water) in small quantities with frequent shaking. The mixture was left for 6 hours at room temperature, acidified with dilute hydrochloric acid and extracted with a large quantity of ether. On distilling off the solvent colourless glistening crystals separated. The dihydroxy compound crystallised from water as colourless prismatic needles melting at 208–9°. Yield, 0·39 g. (Found: C, 59·3; H, 4·0; $C_{11}H_{10}O_5$ requires C, 59·5; H, 4·5.)

The substance gives an emerald green colour with alcoholic ferric chloride.

3:7:8-*Trimethoxy*-2-*methyl chromone* (*XVIII*)

The dihydroxy chromone (0·57 g.) was dissolved in dry acetone (30 c.c.), dimethyl sulphate (0·54 c.c.) and ignited potassium carbonate (3 g.) were added and the mixture gently refluxed over a water-bath for 8 hours. The trimethyl ether after isolation was crystallised from water when it was obtained as colourless flat needles melting at 112–3° after drying in the vacuum. (Found: C, 63·0; H, 5·7; $C_{13}H_{14}O_5$ requires C, 62·4; H, 5·6.)

2-*Hydroxy*-3:4:6-*trimethoxy acetophenone* (*XI*)

This ketone was prepared by the method of Baker.[8] The only modification introduced was in the preparation of pyrogallol trimethyl ether where the methylation was done under a layer of petroleum ether thus obviating the necessity of having an inert gas atmosphere in a gas-tight vessel. The product was quite colourless and was readily obtained.

2-*Hydroxy*-3:4:6-*trimethoxy*-ω-*acetyl acetophenone* (*XII*)

The above ketone (2 g.) was dissolved in ethyl acetate (20 c.c.) and the solution was added in two lots to powdered sodium (1 g.) just covered with a layer of dry ether. When the initial reaction was over the mixture was heated under reflux in a water-bath when the pale yellow sodium salt began to separate in about twenty minutes. After heating for about an hour more ethyl acetate (20 c.c.) was added and refluxing continued for another 3 hours. The mixture was then cooled, the yellow sodium salt was dissolved in ice-cold water (150 c.c.) and the brownish-red solution separated from the layer of ethyl acetate. The aqueous solution was acidified with glacial acetic acid till a turbidity appeared when the diketone separated as a pale

yellow oil which solidified on adding a little petroleum ether. The mixture was left in the refrigerator overnight, the pale yellow solid filtered and crystallised from a mixture of chloroform and ether; the diketone was obtained as light fawn-coloured plates melting at 123-24°. The substance gave a violet-brown colour with alcoholic ferric chloride. Yield, 1·6 g. (Found: C, 58·7; H, 5·7; $C_{13}H_{16}O_6$ requires C, 58·2; H, 6·0.)

5:7:8-*Trimethoxy-2-methyl chromone* (*X*)

The above diketone was crystallised by refluxing a solution of the substance (1·4 g.) in absolute alcohol (10 c.c.) containing 2 drops of concentrated sulphuric acid for 15 minutes. The mixture was cooled, diluted with water (60 c.c.) and made just alkaline with sodium hydroxide solution. It was extracted with chloroform (3 × 10 c.c.) and the trimethoxy chromone was obtained as a colourless solid by removing the solvent. It crystallised from a mixture of chloroform and ether as colourless needles melting at 170–71°. Yield, 1·2 g. (Found: C, 62·0; H, 5·1; $C_{13}H_{14}O_5$ requires C, 62·4; H, 5·6.)

*Demethylation of* 5:7:8-*trimethoxy-2-methyl chromone* (*X*): *Preparation of* 5:6:7-*trihydroxy-2-methyl chromone* (*XIII*)

The trimethoxy chromone (1 g.) was dissolved in acetic anhydride (15 c.c.) and the cooled solution was treated cautiously with hydriodic acid (20 c.c., d. 1·7). The solution was refluxed in an oil-bath at 140° for two hours, then treated with ice-water and the free iodine removed by adding sodium sulphite solution. On standing for about two hours a white powder separated. This was collected, washed several times with water and crystallised from alcohol (in which it was moderately soluble) when the trihydroxy chromone was obtained as fine leaflets having a very pale yellow colour. It melted at 284–86° with slight sintering at 280°. Yield, 0·8 g. (Found: C, 57·8; H, 4·0; $C_{10}H_8O_5$ requires C, 57·7; H, 3·9.) The compound gave an intense bluish-green colour with ferric chloride in alcoholic solution.

*Methylation of the demethylated product*: *Preparation of* 5:6:7-*trimethoxy-2-methyl chromone* (*XIV*)

The demethylated product (0·47 g.) was dissolved in dry acetone (75 c.c.), treated with excess of dimethyl sulphate (1 c.c., 4 mols.) and anhydrous potassium carbonate (6 g.) and the mixture was gently refluxed on a water-bath for 12 hours. The acetone solution was then filtered from the inorganic salts and the solvent removed when a brownish oil was left behind. By adding water it dissolved to a clear brown solution; this was allowed to stand for about two days to decompose all dimethyl sulphate.

The solution was made alkaline with a few drops of aqueous sodium hydroxide and extracted with ether. On removal of the solvent the trimethoxy chromone was left behind as a brown oil which solidified on the addition of a little ethyl acetate-petrol mixture and cooling. It was filtered and recrystallised several times from ethyl acetate-petroleum ether mixture when the trimethyl ether was obtained as starry bunches of colourless needles melting at 99–100°. The melting point was not depressed on admixture with an authentic sample of 5:6:7-trimethoxy-2-methyl chromone (described below). (Found: C, 62·3; H, 5·3; $C_{13}H_{14}O_5$ requires C, 62·4; H, 5·6.)

*2-Hydroxy-4:5:6-trimethoxy-ω-acetyl acetophenone*

2-Hydroxy-4:5:6-trimethoxy acetophenone (XV)[5] (3 g.) was dissolved in ethyl acetate (25 c.c.), the solution was added to powdered sodium (1·5 g.) and the mixture refluxed on a water-bath. The solution turned deep brown and sodium went into solution slowly. After an hour more sodium (0·5 g.) and ethyl acetate (10 c.c.) were added and the heating continued for another 3 hours. The excess of ethyl acetate was then distilled off under reduced pressure, the brownish gummy mass dissolved in ice-water and the solution filtered from a small quantity of undissolved fluffy matter. The clear aqueous solution was acidified with glacial acetic acid till a turbidity appeared; the mixture was left in the refrigerator overnight when a mass of pale cream-coloured crystals separated. These were filtered, washed with a little ether and crystallised from ethyl acetate when the diketone was obtained as pale cream-coloured glistening plates melting at 141–42°. Yield, 2·4 g. (Found: C, 58·5; H, 6·3; $C_{13}H_{16}O_6$ requires C, 58·2; H, 6·0). The compound gave a brown colour with alcoholic ferric chloride.

5:6:7-*Trimethoxy-2-methyl chromone* (*XIV*)

The above diketone (0·5 g.) was dissolved in absolute alcohol (10 c.c.) and 2 drops of concentrated sulphuric acid were added to it. The mixture was heated under reflux for 15 minutes, the pale violet-coloured solution was cooled and diluted with ice-water (60 c.c.) and then made alkaline with a few drops of sodium hydroxide solution. The alkaline solution was extracted with ether and the solvent evaporated when the trimethoxy chromone was obtained as a pale yellow oil which turned into colourless solid on the addition of a little petroleum ether and cooling. It crystallised from ethyl acetate-petroleum ether mixture as starry bunches of colourless needles melting at 99–100°. Yield, 0·4 g. (Found: C, 62·3; H, 5·3; $C_{13}H_{14}O_5$ requires C, 62·4; H, 5·6.)

SUMMARY

Methods of nuclear oxidation are applied for the preparation of chromone derivatives, many of which have been required for the study of isomeric change. Just as in the flavone group the presence of a methoxyl (hydroxyl) in the 3-position prevents isomeric change from the 5:7:8 to the 5:6:7 arrangement of hydroxyl groups; in its absence the isomeric change takes place.

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# THE THEORY OF REDOXO-KINETIC EFFECT

## A CORRECTION

*(Vide Proc. Ind. Acad. Sci., 1951, 34, 263)*

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Received December 13, 1951

IN getting equation (18), the term

$$\text{“ } n\text{FA}k\text{C}\,(2\alpha - 1) \cdot \frac{v^2n^2\text{F}^2}{2\text{R}^2\text{T}^2}\text{ ”}$$

was neglected as it was a second order term. A more careful examination has shown that this has to be taken into account. On doing this, equation (27) becomes

$$\psi = -\,(\alpha - \cdot 5)\,\frac{\text{V}^2n\text{F}}{2\text{RT}}\,\frac{1}{k}\sqrt{\frac{\omega\text{D}}{2}}\;\frac{\dfrac{1}{k}\sqrt{\dfrac{\omega\text{D}}{2}} + 1}{2 + \dfrac{1}{k^2}\cdot\dfrac{\omega\text{D}}{2} + \dfrac{2}{k}\sqrt{\dfrac{\omega\text{D}}{2}}}$$

Equation (28) becomes

$$\psi = -\,(\alpha - \cdot 5)\,\frac{\text{V}^2n\text{F}}{2\text{RT}}\cdot\frac{1}{2k}\sqrt{\frac{\omega\text{D}}{2}}$$

and equation (29) becomes

$$\psi = -\,(\alpha - \cdot 5)\cdot\frac{\text{V}^2n\text{F}}{2\text{RT}}\cdot$$

The general conclusions given on p. 267 below equation (29) are accordingly to be written as follows:—

(*a*) $\psi$ is proportional to $\text{V}^2$ when $\omega$ is constant,

(*b*) At sufficiently *high* frequencies $\psi$ is independent of frequency,

(*c*) At low frequencies,

$\psi$ is *directly* proportional to $\sqrt{\omega}$,

(*d*) At zero frequency

$\psi$ becomes zero.

It is interesting to note, that the fact that $\alpha$ can be determined remains unaltered. The values of $\alpha$ given in the paper would have to be recalculated by applying equation (29) as given in this correction note. This calculation has been postponed, since the values given in the paper are only tentative.

# NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

## Part XXXVI. Oxidation of Some Hydroxy Isoflavones

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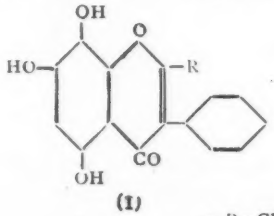
Received November 24, 1951

In the earlier publications of this series[1] the application of two processes of nuclear oxidation to the flavone group and certain related compounds was described in detail. The first is the single stage process using alkaline persulphate and it introduces the hydroxyl group satisfactorily in the position para to an activating hydroxyl group. It is however not satisfactory for ortho oxidation. The two-stage process involving an ortho-hydroxy-aldehyde as an intermediate and its oxidation with hydrogen peroxide is quite satisfactory. Though the preparation of *p*-hydroxy-aldehyde is easy, its oxidation with hydrogen peroxide to yield the corresponding para dihydroxy compound is not satisfactory[2] and the two stage process is not therefore efficient for para oxidation. The two processes would therefore appear to be complimentary to each other.

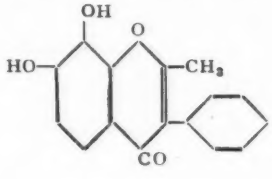
As far as our present knowledge goes, isoflavones do not exhibit such a large range of structural variations as the flavones and flavonols. Still there are indications that nuclear oxidation plays an important part in the evolution of certain members of these groups also, *e.g.*, 5 : 6 : 7-trihydroxy type is found in irigenin and tectorigenin. In this paper are described experiments testing the applicability of nuclear oxidation methods to isoflavones. They are found to work satisfactorily and 5 : 7 : 8-trihydroxy-2-methyl isoflavone (I *a*), 5 : 7 : 8-trihydroxy isoflavone (I *b*) and 7 : 8-dihydroxy-2-methyl isoflavone (II) and their derivatives are prepared and described.




(I)

*a*, R = $CH_3$

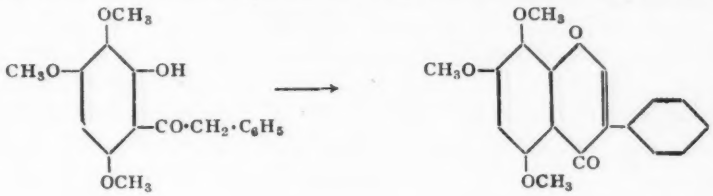
*b*, R = H




(II)

Another object of the present work is to test the possibility of the isomerisation of the 5:7:8-trihydroxy isoflavone into the isomeric 5:6:7-trihydroxy compound by the action of hydriodic acid. This type of isomeric change is known to take place very readily with flavones having 5:7:8-trihydroxy grouping and not with flavonol derivatives.[3] The position is similar in 2-methyl chromone derivatives. It has recently been shown that the methyl ether of 2-methyl-5:7:8-trihydroxy chromone undergoes isomeric change on boiling with hydriodic acid whereas the corresponding 3-methoxy compound does not.[4] It is now found that 2-methyl-5:7:8-trimethoxy isoflavone yields the corresponding trihydroxy compound on demethylation with hydriodic acid. The result has been confirmed by remethylation whereby the original trimethyl ether is obtained. Consequently it is clear that even a phenyl group in the 3-position is capable of preventing this isomeric change.

The above experiments do not however provide information about the influence of substitution in the 2-position. In all the hitherto known cases where the isomeric change was prevented, this position contained a phenyl or methyl group in addition to substitution in the 3-position. In order to clarify this point 5:7:8-trimethoxy isoflavone (IV) has now been prepared from 2-hydroxy-3:4:6-trimethoxy-phenyl-benzyl ketone (III) by condensation with ethyl formate and demethylated with hydriodic acid and with anhydrous aluminium chloride. Both methods yield the same trihydroxy isoflavone giving reactions agreeing with the expected behaviour of 5:7:8-trihydroxy compounds. Further, persulphate oxidation of 5:7-dihydroxy isoflavone yields the same product and both samples give identical derivatives. Hence there is no doubt that substitution in the 2-position has no influence and that the 3-position alone is important.




(III) (IV)

## EXPERIMENTAL

### 5:7:8-*Trihydroxy-2-methyl-isoflavone* (*I a*)

5:7-Dihydroxy-2-methyl isoflavone (1·4 g.) was dissolved in 4% aqueous sodium hydroxide (50 c.c.) and potassium persulphate solution (2 g. in 50 c.c.) was added dropwise with stirring during the course of two hours. The

solution was kept between 15–20° throughout the addition. After 24 hours, the solution was neutralised to litmus with dilute hydrochloric acid. A pale yellow precipitate of the unreacted dihydroxy isoflavone separated out. It was filtered and the filtrate extracted with ether twice to remove the last traces of it. The aqueous solution was then treated with concentrated hydrochloric acid (25 c.c.) and sodium sulphite (1 g.) and heated on the water-bath for 20 minutes. A pale brown crystalline solid separated out on cooling. It was crystallised from alcohol when the 5:7:8-trihydroxy-2-methyl isoflavone separated out in the form of pale yellowish brown elongated needles melting at 204–5°. Yield 0·4 g. (Found in a sample dried at 110° for 3 hours: C, 67·7,; H, 4·2; $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2%.) Its alcoholic solution developed dark olive green colour with ferric chloride changing slowly to dark brown and a brown red colour with *p*-benzoquinone. It dissolved in aqueous alkali producing a bright yellow colour changing rapidly into brown, pink, bluish violet and finally to pale yellow after 15 minutes. It readily dissolved in 5% aqueous sodium carbonate giving a reddish brown solution changing to pale yellow. In concentrated sulphuric acid it gave a yellowish red colour with no fluorescence.

The triacetate obtained by heating the isoflavone (I *a*) with acetic anhydride and sodium acetate crystallised from alcohol as colourless prismatic rods melting at 220–21°. (Found in sample dried at 100° for 3 hours: C, 64·5; H, 4·1; $C_{22}H_{18}O_8$ requires C, 64·4; H, 4·4%.)

*Methylation.*—The trihydroxy-2-methyl isoflavone (0·3 g.) was methylated by refluxing with dimethyl sulphate (1 c.c.) and anhydrous potassium carbonate (5 g.) in dry acetone medium (100 c.c.). After 15 hours another lot of dimethyl sulphate (1 c.c.) was added and refluxing continued for 15 hours more. The acetone was then distilled off and water added to the residue. A semi-solid mass separated out which gradually solidified in the course of a few hours. The solid was filtered and crystallised from alcohol. The trimethyl ether separated in the form of transparent stout rectangular prismatic rods melting at 92–3°. (Found: C, 69·9; H, 5·8; $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·5%.) It was insoluble in alkali and gave no colour with alcoholic ferric chloride.

*Demethylation of 5:7:8-trimethoxy-2-methyl isoflavone*

The trimethyl ether described above (0·3 g.) was demethylated with hydriodic acid and the product worked up as given later for an analogous case. It crystallised from alcohol as needles melting at 204–205° (0·15 g.). It was identical in every respect with 5:7:8-trihydroxy-2-methyl isoflavone des-

cribed above and the mixed melting point was undepressed. On remethylation it produced the original trimethyl ether, m.p. and mixed m.p. 92–93°.

7: 8-*Dihydroxy-2-methyl isoflavone* (*II*)

(i) *Oxidation of 7-hydroxy-2-methyl-isoflavone-8-aldehyde.*—A solution of the aldehyde[5] (0·7 g.) in aqueous alkali (N/2, 6 c.c.) was treated dropwise with hydrogen peroxide (5%, 3 c.c.) in the course of 15 minutes with stirring. During the addition, the solution was kept at the room temperature by cooling in water. Within half an hour a pale yellow solid began to separate out. After 3 hours the mixture was acidified with hydrochloric acid while cooling. The solid product was then filtered and crystallised twice from alcohol when the dihydroxy isoflavone came out in the form of pale yellow rectangular plates melting at 227–8°. Yield 0·5 g. (Found: C, 66.8; H, 4·7; $C_{16}H_{12}O_4$, $H_2O$ requires C, 67·1; H, 4·9%). It dissolved in aqueous alkali yielding a stable yellow solution. Ferric chloride developed a bright green colour in alcoholic solution. Its solution in concentrated sulphuric acid was yellow without fluorescence. It was easily soluble in acetone and alcohol.

(ii) *Oxidation of 7-hydroxy-2-methyl isoflavone.*—To a continuously stirred solution of 7-hydroxy-2-methyl isoflavone (3·5 g.) in aqueous alkali (4%, 100 c.c.), a solution of potassium persulphate (4·2 g. in 75 c.c. of water) was added dropwise in the course of 3 hours. After 24 hours, the product was worked up as in similar cases. It crystallised from alcohol in the form of pale yellow prismatic plates melting at 227–8°. Yield 0·2 g. It was identical with 7: 8-dihydroxy-2-methyl isoflavone obtained by method (i) and the mixed melting point was undepressed.

*Methylation.*—The dihydroxy isoflavone (0·4 g.) was refluxed in dry acetone (60 c.c.) with dimethyl sulphate (0·8 c.c.) and anhydrous potassium carbonate (2 g.) for 10 hours and the product worked up. The dimethyl ether crystallised from alcohol as colourless hexagonal prisms melting at 133–4°. Yield 0·3 g. (Found: C, 72·8; H, 5·0; $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%). It gave no colour with ferric chloride and was insoluble in aqueous alkali.

2-*Hydroxy*-3 : 4 : 6-*trimethoxy-phenyl-benzyl ketone* (*III*)

Anhydrous aluminium chloride (15 g.) was dissolved in dry ether (200 c.c.) with cooling and to the solution was added 1 : 2 : 3 : 5-tetramethoxy benzene (8 g.) in dry ether. The mixture was then treated with phenyl acetyl chloride (8 g.) while cooling in ice and the reaction mixture was kept in the ice-bath for 2 hours and at room temperature for 12 hours. Ether was

removed on a warm water-bath, the remaining organo-aluminium complex first treated with ice and hydrochloric acid and subsequently heated on a water-bath to complete the hydrolysis. The solid that separated on cooling was filtered and washed with water. It was purified by dissolving it in aqueous sodium hydroxide, filtering the solution and reprecipitating it by acidification. 2-Hydroxy-3 : 4 : 6-trimethoxy-phenyl-benzyl ketone crystallised from alcohol in the form of colourless broad rectangular plates melting at 86–7°. It gave a deep red colour with ferric chloride. (Found : C, 67·6; H, 6·2; $C_{17}H_{18}O_5$ requires C, 67·5; H, 6·0%.)

5 : 7 : 8-*Trimethoxy isoflavone* (*IV*)

Pulverised sodium (1 g.) cooled in ice, was treated with a solution of 2-hydroxy-3 : 4 : 6-trimethoxy-phenyl-benzyl ketone (2 g.) in dry ethyl formate (10 c.c.). The mixture was kept in the refrigerator for 24 hours at the end of which pieces of ice were added to the reaction mixture. On removing the excess of ethyl formate under reduced pressure a colourless crystalline solid separated. Acidification of the aqueous solution gave a little more of it. It was filtered, washed with water and crystallised from alcohol. On recrystallising from ethyl acetate, 5 : 7 : 8-trimethoxy isoflavone separated as colourless stout rectangular prisms melting at 146–7°. It gave no colour with ferric chloride and was insoluble in aqueous sodium hydroxide. Yield, 1·2 g. (Found : C, 65·7; H, 5·7; $C_{18}H_{16}O_5$, $H_2O$ requires C, 65·4; H, 5·7%.)

5 : 7 : 8-*Trihydroxy isoflavone* (*I b*)

(i) *By demethylation with hydriodic acid.*—An acetic anhydride solution of 5 : 7 : 8-trimethoxy isoflavone (1 g. in 5 c.c.) was treated with cooling with hydriodic acid (sp. gr. 1·7, 10 c.c.) and the mixture heated in an oil-bath at 140° for 3 hours. It was then cooled and diluted with sulphur dioxide water. The bright yellow solid that separated was filtered, washed with water and crystallised from alcohol. On recrystallising from ethyl acetate it was obtained as shining yellow thin plates melting at 280–2°. It gave a green colour changing to brown slowly with ferric chloride in alcohol and a yellow solution changing to brown with aqueous sodium hydroxide. It was identical in its properties with the samples of 5 : 7 : 8-trihydroxy isoflavone described below and the mixed melting points were undepressed. (Found : C, 66·2; H, 4·0; $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7%.)

The triacetate crystallised from alcohol as colourless needles melting at 206–8° and the mixed melting point with the acetate sample described

later (expt. iii) was undepressed. (Found: C, 64·0; H, 4·4; $C_{21}H_{16}O_8$ requires C, 63·6; H, 4·0%.)

(ii) *By persulphate oxidation.*—A stirred solution of 5:7-dihydroxy isoflavone (1·7 g.) in sodium hydroxide (20 c.c., 1 N) was treated with sodium persulphate solution (4 g. in 30 c.c. water) during the course of 3 hours the temperature being maintained between 15 and 20°. After 24 hours the solution was acidified to congo-red and the unchanged dihydroxy isoflavone filtered off and finally extracted with ether. The aqueous solution was then treated with sodium sulphite (1 g.) and concentrated hydrochloric acid (20 c.c.), heated to 90° on a water-bath and allowed to cool gradually when a yellow solid separated. After leaving overnight the product was filtered, washed with water and crystallised from alcohol when it was obtained in the form of bright yellow plates melting at 280–2°. It gave a green colour changing to brown with alcoholic ferric chloride and agreed in all its properties with samples obtained by other methods. Yield, 0·5 g.

(iii) *By demethylation with aluminium chloride.*—The trimethoxy isoflavone (0·2 g.) was dissolved in dry benzene (10 c.c.), treated with anhydrous aluminium chloride (1 g.) and the mixture refluxed on a water-bath for 2 hours. Benzene was then removed on a boiling water-bath and the residue treated with ice and hydrochloric acid. The mixture was warmed on a water-bath for a few minutes, cooled and the solid product filtered. It crystallised from alcohol as yellow thin plates melting at 280–2° and agreed in its properties with the compound obtained in the above experiments and the mixed melting point showed no depression. On acetylation the triacetate was obtained which crystallised from alcohol in the form of colourless needles melting at 206–8°.

5-*Hydroxy*-7:8-*dimethoxy isoflavone*

5:7:8-Trihydroxy isoflavone (obtained by demethylation with hydriodic acid in expt. i) (0·3 g.) was partially methylated by heating with dimethyl sulphate (0·25 c.c.) and anhydrous potassium carbonate (1 g.) in acetone solution for 6 hours. On filtering and removing the solvent from the filtrate the product separated as a yellow solid. It crystallised from alcohol as pale yellow prisms melting at 156–7°. It gave a green colour with ferric chloride and was sparingly soluble in aqueous alkali. It was identical with a similar derivative prepared from the sample obtained by oxidation with persulphate (in exp. ii). (Found: C, 68·0; H, 4·7; $C_{17}H_{14}O_5$ requires C, 68·5; H, 4·7%.)

## SUMMARY

Using methods of nuclear oxidation 7: 8-dihydroxy-2-methyl isoflavone, 5: 7: 8-trihydroxyisoflavone and 5: 7: 8-trihydroxy-2-methyl isoflavone and their derivatives have been prepared. Demethylation of the 5: 7: 8-trimethoxy isoflavones with or without a 2-methyl group does not produce isomeric change in the trihydroxy product. It could therefore be concluded that a phenyl group in the 3-position prevents this isomeric change just like a methoxyl (hydroxyl) in the same position and that substitution in the 2-position has no influence.

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# A NOTE ON THE GENERALISED LAGUERRE POLYNOMIAL

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Received November 19, 1951
(Communicated by Prof. B. S. Madhava Rao, F.A.Sc.)

1. The generalised Laguerre polynomial

$$L_n^{(\alpha)}(z) = \frac{e^z z^{-\alpha}}{n!}\left(\frac{d}{dz}\right)^n (e^{-z} z^{n+\alpha}),$$

where $\alpha > -1$ and $n$ is an integer $\geqslant 0$, is a solution of the following differential and functional equations:

$$z\frac{d^2 f_n(z)}{dz^2} + (\alpha + 1 - z)\frac{df_n(z)}{dz} + nf_n(z) = 0., \tag{1}$$

$$nf_n(z) - (2n + \alpha - 1 - z)f_{n-1}(z) + (n + \alpha - 1)f_{n-2}(z) = 0 \tag{2}$$

$$f'_n(z) = f'_{n-1}(z) - f_{n-1}(z) \tag{3}$$

$$(n + \alpha - z)f'_n(z) = (n + \alpha)f'_{n-1}(z) - nf_n(z) \tag{4}$$

$$zf'_n(z) = nf_n(z) - (n + \alpha)f_{n-1}(z). \tag{5}$$

It is easy to verify that these are equivalent to two independent equations only.

Consider now the series

$$V = \sum_{n=0}^{\infty} h^n f_n(z), \tag{6}$$

where $f_n(z)$ is an analytic solution of (2). When $|h| < R$, the radius of convergence of the power series (6),

$$\frac{\partial V}{\partial h} = \sum_{n=0}^{\infty} nh^{n-1} f_n(z). \tag{7}$$

Multiplying (2) by $h^{n-1}$ and summing up for $n = 2, 3, 4, \ldots$, we get

$$\sum_{n=2}^{\infty} nh^{n-1} f_n(z) = 2\sum_{n=2}^{\infty} nh^{n-1} f_{n-1}(z) + (\alpha - 1 - z)\sum_{n=1}^{\infty} h^{n-1} f_{n-1}(z)$$

$$- \sum_{n=2}^{\infty}(n-1)h^{n-1} f_{n-2}(z) - \alpha\sum_{n=2}^{\infty} h^{n-1} f_{n-2}(z),$$

which can be written, by using (6) and (7), as

$$\frac{\partial V}{\partial h} + \frac{(\alpha+1)h - A}{(1-h)^2} V = \frac{B}{(1-h)^2}, \tag{8}$$

where $A = \alpha + 1 - z$ and $B = f_1(z) - A f_0(z)$.

Solving (8), we get

$$V = \frac{B\int_0^h (1-h)^{\alpha+1} e^{\frac{z}{1-h}}\, dh + \psi(z)}{(1-h)^{\alpha+1} e^{\frac{z}{1-h}}}, \quad (|h| < R). \tag{9}$$

To determine $\psi(z)$, take the particular value $h = 0$. Then (9) gives

$$\psi(z) = e^z f_0(z).$$

The value of the radius of convergence R is obtained by applying Van Vleck's theorem[1] on Linear Criteria for the determination of the radius of convergence of a power series. From (2),

$$f_{n+2}(z) = p_n f_{n+1}(z) + q_n f_n(z)$$

where $p_n = \dfrac{2n + \alpha + 3 - z}{n+2}$ and $q_n = -\dfrac{n+1+\alpha}{n+2}$.

Since $p_n \to 2$, $q_n \to -1$ (when $n \to \infty$), R is equal to the coincident root of the quadratic $k^2 - 2k + 1 = 0$, *i.e.*, $R = 1$. We thus have:

*If $f_n(z)$ be any analytic solution of the difference equation*

$$(n+1) f_{n+1}(z) - (2n + \alpha + 1 - z) f_n(z) + (n + \alpha) f_{n-1}(z) = 0$$

*and the point '$h$' is inside the unit circle with centre at the origin, then*

$$\sum_{n=0}^{\infty} h^n f_n(z) = \frac{\{f_1(z) - (\alpha + 1 - z) f_0(z)\} \int_0^h (1-t)^{\alpha+1} e^{\frac{z}{1-t}}\, dt + e^z f_0(z)}{(1-h)^{\alpha+1} e^{\frac{z}{1-h}}} \tag{10}$$

*the line-integral being taken along any Jordan curve connecting* O *and '$h$'.*

3. If we set $f_0(z) = L_0^{(\alpha)}(z) = 1$, $f_1(z) = L_1^{(\alpha)}(z) = \alpha + 1 - z$, the formula (10) leads to the result[2]

$$\sum_{n=0}^{\infty} h^n . L_n^{(\alpha)}(z) = (1-h)^{-(\alpha+1)} e^{-\frac{zh}{1-h}}, \quad (|h| < 1). \tag{11}$$

If $F(z)$ admits of a uniformly convergent expansion of the type

$$F(z) = \sum_{n=0}^{\infty} A_n L_n^{(\alpha)}(z),$$

it is known that[3]

$$A_n = \frac{n!}{\Gamma(n+\alpha+1)} \int_0^{\infty} e^{-x} x^{\alpha} F(x) L_n^{(\alpha)}(x)\, dx.$$

Taking $F(z) = e^{\frac{-zh}{1-h}}$, we obtain[4] from (11),

$$\int_0^{\infty} e^{-\frac{x}{1-h}} x^{\alpha} L_n^{(\alpha)}(x)\, dx = \frac{\Gamma(n+\alpha+1)}{n!} h^n (1-h)^{\alpha+1}.$$

## References


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1171-81—Printed at The Bangalore Press, Bangalore City, by G. Srinivasa Rao, Superintendent
and Published by The Indian Academy of Sciences, Bangalore